NUCLEAR SPIN-LATTICE RELAXATION STUDIES IN LIQUIDS

Thesis by

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In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1974

(Submitted August 3, 1973)

Acknowledgments

The author wishes to thank Professor Sunney I. Chan for his patience and support.

I gratefully acknowledge financial support from the California Institute of Technology and the National Science Foundation.

I am indebted to Jerry Feigenson for helpful discussions in connection with Part III of this thesis.

Finally, I wish to thank all of my friends for making my stay at Caltech enjoyable.

ABSTRACT

In order to study and better understand the microdynamic behavior of liquids, the nuclear spin-lattice relaxation rate has been measured and calculated for fluorine-19 in trifluoroacetic acid, and calculated for carbon-13 in toluene, carbon disulfide, benzene, methyl iodide, acetonitrile, and n-decane.

For fluorine in trifluoroacetic acid it is shown that the relaxation is controlled by the spin-internal-rotation interaction.

Spin-internal-rotation coupling is also shown to be important for carbon-13 relaxation of the methyl carbon of toluene, although intramolecular dipolar coupling also makes a significant contribution.

For carbon disulfide, it is shown that while the anisotropic chemical shift mechanism will contribute to the relaxation rate at superconducting magnetic fields, the spin-rotation interaction provides the dominant mechanism.

For benzene, it is shown that motion about the C_6 symmetry axis can best be described using the inertial model. Intramolecular dipolar coupling is seen to be more important than spin-rotation coupling.

For methyl iodide and acetonitrile, it is shown that a description

in which the motion is taken to be highly anisotropic gives good agreement with experiment.

In Part III, a description of the internal rotation for molecules containing alkane chains is given using the Rotational Isomeric State Approximation. The dynamics of the rotation implied by this model are analyzed, and the results are used to calculate carbon-13 spin-lattice relaxation rates for the methylene carbons. The model appears to be successful in predicting the relaxation time differences for the carbons at the methyl end of n-decanol.

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I. THE THEORY OF NUCLEAR SPIN-LATTICE RELAXATION

1. An Introduction[1, 2]

A nucleus with spin angular momentum $\vec{I}$ has a magnetic moment $\vec{\mu} = \gamma \hbar \vec{I}$, where the proportionality constant is called the gyromagnetic ratio. The application of a magnetic field $\vec{H}$ produces an interaction, for which the Hamiltonian is $\mathcal{H} = -\vec{\mu} \cdot \vec{H}$. If $\vec{H}$ is a static field, defined to be in the z direction in the laboratory frame of reference, then

$$\mathcal{H} = -\mu_z H_0 = -\gamma \hbar H_0 I_z \tag{1}$$

The eigenvalues of this Hamiltonian are simply those of I_z times $-\gamma \hbar H_0$

$$E_m = -\gamma \hbar H_0 M_z \qquad M_z = I, I-1, \ldots, -I \tag{2}$$

For $I = \frac{1}{2}$,

$$E = \pm \frac{\gamma \hbar H_0}{2} \tag{3}$$

The eigenstate for the lower energy state $m = \frac{1}{2}$ (assuming a positive value for γ), for which the magnetic moment and the applied field are parallel, is denoted as $|\alpha>$, while that of the higher energy state $m = -\frac{1}{2}$, for which the field and the magnetic moment are anti-parallel, is denoted by $|\beta>$. In order to induce transitions between these nuclear spin energy levels, we apply an oscillating electromagnetic field with an angular frequency ω such that $\hbar\omega = \Delta E = \gamma \hbar H_0$,

or $\omega = \gamma H_0$. At thermal equilibrium, given a macroscopic system containing a large number N of weakly interacting spins, there will be an excess of spins in the lower energy state $|\alpha>$, a condition which produces a net absorption of energy when the rf field is applied. The distribution of spin population is given by Boltzmann's law:

$$N_\alpha / N_\beta = \exp(\gamma \hbar H_0 / kT) \tag{4}$$

At ordinary temperatures, $\gamma \hbar H_0 \ll kT$, so that the exponential can be expanded as approximately equal to $1 + \gamma \hbar H_0 / kT$. The unequal population distribution gives rise to a resultant macroscopic magnetic moment in the direction of the static applied field. Since the populations can be shown to be approximately

$$\begin{aligned} N_\alpha &= \tfrac{1}{2} N (1 + \gamma \hbar H_0 / 2kT) \\ N_\beta &= \tfrac{1}{2} N (1 - \gamma \hbar H_0 / 2kT) \end{aligned} \tag{5}$$

by defining a mean population $\bar{N} = \frac{1}{2}(N + N)$, the total magnetic moment $\vec{M}$, or the magnetization, as it is called, can be calculated

$$\begin{aligned} \vec{M} &= (N_\alpha - N_\beta)\,\vec{\mu} = N \gamma \hbar H_0 \vec{\mu} / 2kT \\ M_Z^0 &= N \hbar^2 \gamma^2 H_0 / 4kT \end{aligned} \tag{6}$$

for spin $\frac{1}{2}$ nuclei. The individual magnetic moments precess about the applied field direction, but at thermal equilibrium, it is assumed for a statistical ensemble of spins that the phases of the individual spins are distributed randomly, so there is no net magnetization in

the x or y laboratory directions. If we perturb the equilibrium magnetization with a time dependent magnetic field $\vec{H}_1(t)$, the resulting change in the magnetization can be described by the Bloch equation[3]

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H} - \frac{(M_x \vec{i} + M_y \vec{j})}{T_2} - \frac{(M_z - M_z^0)\vec{k}}{T_1} \qquad (7)$$

where $\vec{H} = H_0 \vec{k} + \vec{H}_1(t)$. The first term on the right hand side describes, using the classical description of a magnetic moment in a magnetic field, the precession of the magnetization about the field direction. The second and third terms describe the tendency of $\vec{M}$ to return to the thermal equilibrium value. The application of the $\vec{H}_1$ field at the proper frequency tends to align the individual magnetic moments, producing a net magnetization in the x-y plane. Upon removal of the $\vec{H}_1$ field, the individual moments will dephase, so the x and y components of $\vec{M}$ decay exponentially to zero with a time constant T_2, called the transverse relaxation time. Furthermore, the populations of the spin states, perturbed by the quantum mechanical transitions caused by the $\vec{H}_1$ field, tend to return to their thermal equilibrium values, so that M_z approaches M_z^0 exponentially with a time constant T_1, called the longitudinal or spin-lattice relaxation time. In the usual, continuous-wave nmr experiment, H_1 is weak (~ 0.1 milliGauss), which limits the number of spin transitions, so that relaxation keeps the spin populations close to their equilibrium values. This enables the resonance to be observed

continuously, with its correct lineshape.

We now consider in detail the effect of $\vec{H}_1(t)$. Consider a circularly polarized rf field, which is rotating clockwise in the x-y plane with uniform angular velocity ω,

$$\vec{H}_1(t) = H_1 (\vec{i} \operatorname{Cos} \omega t - \vec{j} \operatorname{Sin} \omega t) \tag{8}$$

To simplify the description of the motion of the magnetization $\vec{M}$ for an $\vec{H}_1$ field of this form, we transform the equation of motion for $\vec{M}$ from the laboratory frame of reference (x, y, z) to a frame of reference (x′, y′, z′) that is rotating about the z axis of the laboratory frame at a frequency ω_0. From classical mechanics the time change of a vector in a fixed coordinate system is related to the time change of the vector in a rotating system by

$$\left.\frac{d\vec{M}}{dt}\right)_{lab} = \left.\frac{\partial \vec{M}}{\partial t}\right)_{rot} + \vec{\omega} \times \vec{M} \tag{9}$$

where $\partial/\partial t$ is used to represent differentiation with respect to the rotating coordinate system. Since $d\vec{M}/dt)_{lab} = \gamma \vec{M} \times \vec{H}$

$$\begin{aligned} \left.\frac{\partial \vec{M}}{\partial t}\right)_{rot} &= \gamma \vec{M} \times \vec{H} + \gamma \vec{M} \times \vec{\omega}/\gamma \\ &= \gamma \vec{M} \times (\vec{H} + \vec{\omega}/\gamma) \\ &= \gamma \vec{M} \times \vec{H}_{eff} \end{aligned} \tag{10}$$

where we have left out the relaxation terms, and where $\vec{H}_{eff}$ is the effective magnetic field about which $\vec{M}$ precesses in the rotating

frame. We now write

$$\vec{H}_{eff} = H_0 \vec{k}' + \vec{\omega}/\gamma + \vec{H}_1')_{rot} \tag{11}$$

In a frame rotating at frequency ω, $\vec{H}_1')_{rot}$ will be static, and can be written $\vec{H}_1' = H_1 \vec{i}'$, with the proper choice of axes. We also note that, because we chose the z′ axis to be in the direction of H_0 (z axis), that $\vec{\omega} = -\vec{k}'\omega$. Therefore

$$\vec{H}_{eff} = \vec{k}' (H_0 - \omega/\gamma) + H_1 \vec{i}' \tag{12}$$

At resonance, $\omega_0 = \omega$, so that $\vec{H}_{eff} = H_1 \vec{i}'$ and

$$\partial \vec{M}/\partial t = \gamma H_1 \vec{M} \times \vec{i}' \tag{13}$$

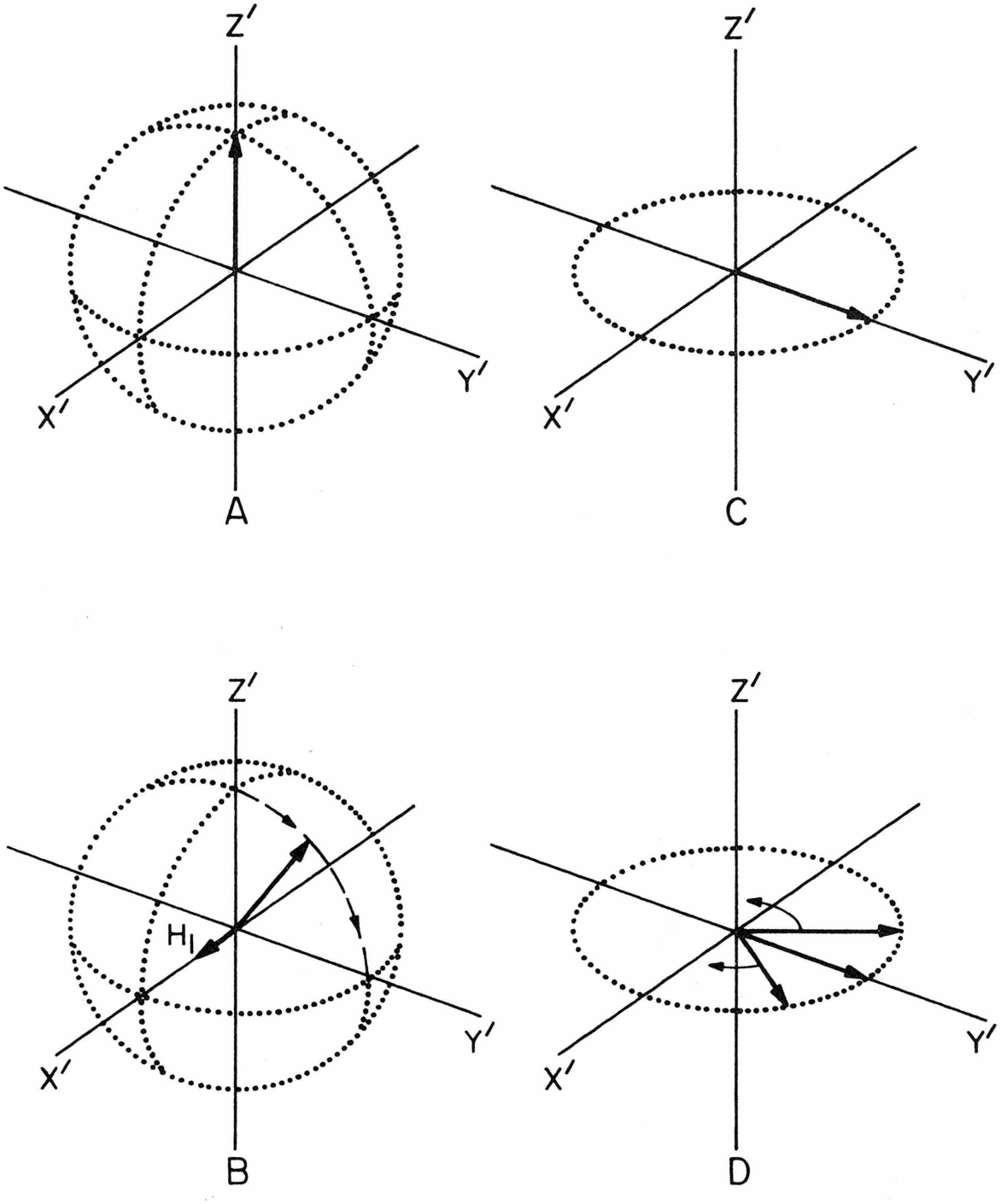
i.e., the magnetization precesses about the x′ axis with frequency $\omega_1 = \gamma H_1$. In the typical liquid state pulsed nmr experiment, H_1 is large (1-10 Gauss), and is applied only for a time t_w, which is short with respect to T_1 and T_2. In a time t_w the magnetization precesses through an angle $\theta = \gamma H_1 t_w$ radians. A so-called 90° pulse, then, has a t_w such that, given H_1, $\theta = \pi/2 = \gamma H_1 t_w$, and will rotate $\vec{M}$ from the z′ axis to the y′ axis. Since the y′ axis is rotating with frequency ω_0 in the laboratory frame, and an nmr spectrometer is normally arranged to detect signals induced by the precessing magnetization in a coil along the x or y axis, the magnitude of $M_{y'}$ determines the strength of the observed signal (called a free induction decay because the spins are precessing "freely" without an applied rf field). As the individual magnetic moments lose phase

coherence, and, as seen in the rotating frame, fan out in the x'-y' plane (Figure 1), $M_{y'}$ decays to zero. The Bloch equation, Eq. (7), indicates that the time constant for the free induction decay is the transverse relaxation time T_2, which is true only if the dephasing effects of the inhomogeneity of the static magnetic field (i.e., different values of H_0 in different parts of the sample cause different precession rates) are included in T_2. However, in practice, because inhomogeneity dephasing usually dominates such that it determines the time constant for the free induction decay, and since this time constant, once known, is not of any further physical significance, its contribution is not included in the T_2 defined in the Bloch equation.

However, in this work, we will primarily be interested in processes which cause spin energy level transitions, i.e., we want to determine the spin-lattice relaxation time T_1, and not T_2. This is because in general the processes that determine T_2 are more complicated than those responsible for T_1, although in many cases, these processes will be the same. Furthermore, the measurement of T_1 is experimentally less difficult than the measurement of T_2. To measure T_1 we first apply to a spin system at thermal equilibrium a 180° pulse ($\pi = \gamma H_1 t_w$), which leaves the magnetization aligned along the -z axis. There is obviously no free induction decay after a 180° pulse. Immediately after the pulse, the system will start to relax longitudinally towards thermal equilibrium. At a time t after the 180° pulse, we apply a 90° pulse, producing a free induction decay whose amplitude is proportional to the value of M_z at the

FIGURE 1

The formation of a free induction decay as viewed from the rotating reference frame. Initially the net magnetization is in its equilibrium position (A) parallel to the direction of the static magnetic field H_0. The pulsed rf field H_1 causes the magnetization to rotate (B) rapidly about H_1. At the end of the 90° pulse the net magnetic moment is in the equatorial plane (C). Following the removal of H_1, the variations in H_0 over the sample cause the isochromats to slowly fan out (D).


Z′
X′
Y′
A
Z′
X′
Y′
C
Z′
H_I
X′
Y′
B
Z′
X′
Y′
D

time of the 90° pulse. If we repeat this experiment, after waiting until the system has reached thermal equilibrium again, for varying times t between the 180° and 90° pulses, we obtain a series of signal amplitudes which describe a curve with the equation (see Figure 2)

$$M_z(t) = M_z^0 \ (1 - 2 \exp(-t/T_1)) \tag{14}$$

which was obtained by solving the Bloch equation

$$dM_z/dt = -(M_z - M_z^0)/T_1 \tag{15}$$

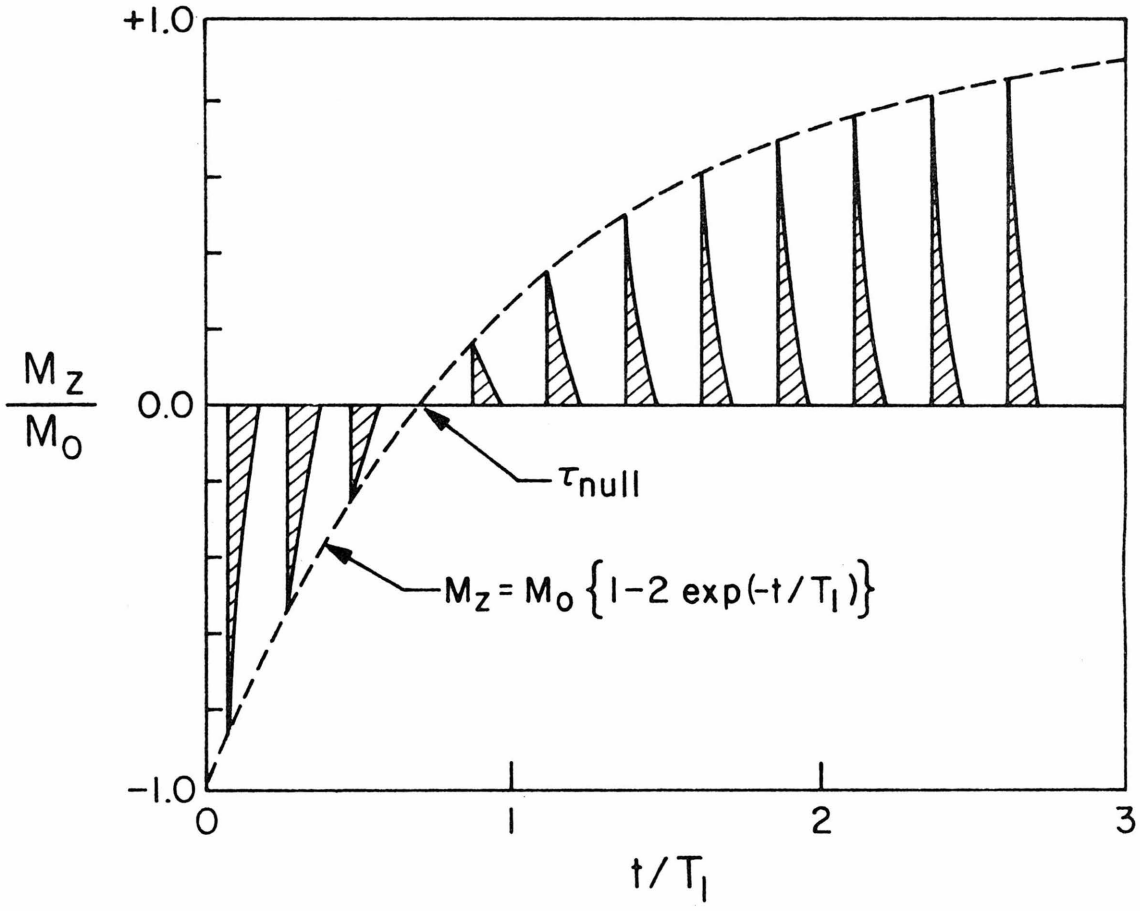
with the boundary condition $M_z(0) = -M_z^0$. At one particular value of t, designated τ_{null}, there will be no free induction decay ($M_z(\tau_{null}) = 0$). Experimentally, we measure τ_{null} and calculate T_1 from $\tau_{null} = T_1 \ln 2$.

2. The BPP Treatment

Bloembergen, Purcell, and Pound (BPP) originally proposed that nuclear spin-lattice relaxation in liquids is due to local molecular magnetic fields and electric fields made time dependent by random molecular motions.[4] Relaxation occurs when the Fourier spectrum of the time-dependent components of the fluctuating fields has a non-vanishing intensity at the frequency ω_0 which corresponds to the frequency of transition between the two energy levels of the nuclear spin system. These transitions bring the non-equilibrium spin system into thermal equilibrium with the surrounding medium

FIGURE 2

A "multiple exposure" of a sequence of T_1 experiments.


+1.0
0.0
-1.0
$\frac{M_z}{M_o}$
τ_{null}
$M_z = M_o \{1-2\exp(-t/T_1)\}$
0
1
2
3
t/T_1

-- the "lattice". Obviously, the spin-lattice relaxation time is directly related to the transition probability between the two spin energy levels. We therefore want to calculate the strength and frequency distribution of the randomly fluctuating local magnetic fields. If $\mathcal{H}(t)$ is a random stationary molecular function, i.e., it fluctuates about some fixed mean value for each molecule, then the usual measure of the variation in $\mathcal{H}(t)$ is the statistical mean square average $\overline{\mathcal{H}^*(t)\,\mathcal{H}(t)}$, where the bar denotes the statistical average. This average will usually have a positive non-zero value. A quantity similar to the statistical average of $\mathcal{H}(t)$ is

$$G(\tau) = \overline{\mathcal{H}^*(t+\tau)\,\mathcal{H}(t)} \tag{16}$$

which is called the autocorrelation function of $\mathcal{H}(t)$. The quantity $\mathcal{H}^*(t+\tau)\,\mathcal{H}(t)$ will be different for each molecule and at each time t, but for many random processes, such as Brownian motion in solution, the mean value $G(\tau)$ will be the same for all molecules and independent of time. In this case $G(\tau)$ will be a measure of the persistence of the fluctuation; it will be large for short times τ, and will decay to zero as τ increases. It is usually assumed that this decay of $G(\tau)$ is exponential with a time constant τ_c,

$$G(\tau) = \overline{\mathcal{H}^*(t)\,\mathcal{H}(t)}\ \exp\left(-|\tau|/\tau_c\right) \tag{17}$$

This assumption can generally be shown to be valid when the time scale of the fluctuations is that of molecular motion in liquids ($\sim 10^{-8}$ sec or less). The correlation time thus characterizes the

motion of the molecule. As mentioned above, we are interested in the frequency spectrum of the fluctuations. The frequency variation of any function $\mathcal{H}(t)$ is given by its Fourier transform

$$\mathcal{H}(\omega) = \int_{-\infty}^{\infty} \mathcal{H}(t) \exp(i\omega t)\, dt \tag{18}$$

but $\mathcal{H}(\omega)$ will also be a random function if $\mathcal{H}(t)$ is. The Fourier transform of the autocorrelation function $G(\tau)$ will be

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(i\omega\tau)\, d\tau \tag{19}$$

The Wiener-Khintchin theorem shows that the quantity $J(\omega)$ is the power generated by the fluctuations of $\mathcal{H}(t)$ at the frequency ω, and so it is called the power spectrum or the spectral density of $\mathcal{H}(t)$. When $G(\tau)$ is given by Eq. (17), the power spectrum of $\mathcal{H}(t)$ will be

$$J(\omega) = \overline{\mathcal{H}^*(t)\,\mathcal{H}(t)}\; 2\tau_c/(1 - \omega^2 \tau_c^2) \tag{20}$$

The statistical average $\overline{\mathcal{H}^*(t)\,\mathcal{H}(t)}$ will be independent of time. Also, for normal sized molecules in solution, where correlation times have been observed to fall in the range 10^{-10}-10^{-14} sec, $(\omega\tau_c)^2 \ll 1$, which is called the extreme narrowing limit, so we have

$$J(\omega) = |\mathcal{H}(0)|^2\, 2\tau_c \tag{21}$$

The transition probability between two quantum states $|\alpha\rangle$ and $|\beta\rangle$ due to a perturbation $\mathcal{H}(t)$ is given by time dependent perturbation theory as

$$\hbar^2 W_{\alpha\beta} = \int_{-\infty}^{\infty} \overline{\langle \beta \,|\, \mathcal{H}(t+\tau) \,|\, \alpha \rangle \langle \alpha \,|\, \mathcal{H}(t) \,|\, \beta \rangle}\, e^{-i\omega_{\beta\alpha}\tau} \qquad (22)$$

where $\omega_{\beta\alpha} = (E_\beta - E_\alpha)/\hbar$. From the definition of $J(\omega)$, we see that

$$W_{\alpha\beta} = J_{\beta\alpha}(\omega)/\hbar^2 \qquad (23)$$

The rate of spin-lattice relaxation for spin $\frac{1}{2}$ nuclei is

$$\begin{aligned} R_1 = 1/T_1 = 2W_{\alpha\beta} &= 2J_{\beta\alpha}(\omega)/\hbar^2 \\ &= |\mathcal{H}_{\beta\alpha}(0)|^2 \, 4\tau_c/\hbar^2 \end{aligned} \qquad (24)$$

where $\mathcal{H}_{\beta\alpha}(0)$ is the matrix element $\mathcal{H}_{\beta\alpha} = \langle \beta \,|\, \mathcal{H}(0) \,|\, \alpha \rangle$. Thus the relaxation rate is proportional to the square of the matrix element of the perturbing function $\mathcal{H}$, and to the time scale of the function's fluctuations.

We can generalize Eq. (24) by writing

$$R_1 = f(\text{lattice})\, \tau_c \qquad (25)$$

where f (lattice) is a function of the "static" properties of the molecule or molecular system under consideration. Writing R_1 in this manner emphasizes its usefulness, that is, from measurements of a macroscopic quantity, the relaxation rate, we can obtain information about the microdynamic behavior of the system, through the correlation time τ_c.

3. Spin-Lattice Relaxation Studies -- A Brief Historical Summary

At this point it is useful to describe in a general manner the way in which relaxation studies are carried out, in an attempt to put the present work in the proper context, and to summarize the theory that will be presented.

The hydrogen nucleus was, historically, the obvious starting point for relaxation studies, because of the abundance of proton containing compounds, the large gyromagnetic ratio of the proton and the fact that it has spin $\frac{1}{2}$, the previous molecular and atomic beam experiments done on hydrogen and proton containing compounds, and because of the relative simplicity of the spin-lattice interactions for protons. Spin-lattice relaxation rates for protons in the liquid state are dominated by the dipole-dipole interaction -- the coupling between the magnetic dipole moment of the proton of interest and those of other nuclei (chiefly other protons), modulated by the motion of the molecule in solution. This dipolar coupling may be either intramolecular or intermolecular. Bloembergen, Purcell, and Pound, in their original nuclear magnetic relaxation study, calculated the intra- and intermolecular dipolar contributions to the relaxation rate for the protons in the water molecule.[4] Starting with the Hamiltonian for the dipole-dipole interaction, they derived the expression for f (lattice). Intramolecular relaxation depends on the change in the angular orientation of the vector joining the two dipoles, so that the intramolecular correlation time depends on the

rotation of the molecule. The fluctuation of the magnetic field due to dipoles in other molecules is mainly due to the relative translation of the molecules, so the intermolecular correlation time must reflect this. BPP modified expressions for the correlation times derived by Debye for dielectric relaxation. They obtained reasonably good agreement between the theory and experiment.[4] In subsequent proton relaxation studies, it was determined that the discrepancies between theory and experiment are largely due to inadequacies in the models for the intramolecular correlation time. It was shown that the intermolecular dipolar relaxation rate could be calculated to satisfactory accurary (± 10 %) using existing models for the translational correlation time.[5] Relaxation studies for protons thus consisted chiefly of separating out the intermolecular dipolar contribution, either experimentally or theoretically, calculating f (lattice) using known bond distances, calculating experimental values for the intramolecular correlation time from T_1 data, and comparing these values with those calculated using various models and corrections. This was sometimes done as a function of temperature, pressure, solvent or other variables.

An additional important use for experimental correlation time values is to use them to obtain information about the microdynamic behavior of solvation spheres.[6] By measuring T_1 of water protons as a function of temperature and the concentration of diamagnetic ions in solution, we can calculate lifetimes of the water molecules in the solvation spheres of the ions, and activation

energies for solvation.

Fluorine-19 has a gyromagnetic ratio that is nearly as large as that of the proton, and is found in a variety of simple molecules, so a logical extension of the proton work was to measure fluorine-19 relaxation rates, and apply the theory that had been developed for protons. However, it was found that an additional relaxation mechanism, the spin-rotational interaction, is often important for fluorine-19, particularly for small molecules.[7] This interaction is due to the coupling between the nuclear spin angular momentum and the magnetic field created by the rotation of the electron and nuclear charges in the molecule. Unfortunately, the angular momentum coupling constant between the spin and the molecule is difficult to measure, except for very simple molecules using molecular beam techniques. Also, the correlation time for the spin-rotational interaction is not the same as the correlation times for the dipolar interactions, since it depends on the reorientation of the angular momentum of the molecule. For these reasons, and the lack of an adequate, widely applicable model for the correlation time for angular reorientation, the quantitative separation of the contributions was all but impossible, and the evaluation of different models for f (lattice) and τ_c for the spin-rotational interaction difficult.

A similar situation existed for phosphorous-31 ($I = \frac{1}{2}$), for which the spin-rotational interaction is also important.[8]

This situation, in which there was little progress being made in relaxation studies, persisted until about 1968. Since that point,

however, several theoretical and experimental developments have made possible fairly rapid progress. Possibly the most important among these is the work of Huntress and co-workers.[9-13] In work previous to this, it was generally assumed that the motion of the molecules in solution is isotropic. However, it was shown that, for molecules that are not approximately spherical tops, this is not a good approximation. Huntress used the most general form of the diffusion equation to obtain expressions for the relaxation rate for the various mechanisms for a molecule undergoing anisotropic rotational diffusion.[9]

It had often been pointed out in the literature, that nuclei with spin angular momentum greater than $\frac{1}{2}$, i. e., those with an electric quadrupole moment, can relax through the interaction of the moment and the molecular electric field gradient at the nucleus, when the interaction is modulated by random molecular motion. Furthermore, for most quadrupolar nuclei, this mechanism dominates to the exclusion of all other mechanisms. There is also no translational contribution to quadrupolar relaxation. Thus the difficulties of having several contributing mechanisms are avoided. However, this knowledge was not effectively utilized until Huntress and co-workers combined it with their work on anisotropic diffusion, and demonstrated that, by measuring the relaxation rates of quadrupolar nuclei with the proper orientation with respect to the principal inertial axes of the molecule, the three principal rotational diffusion coefficients for the molecule could be determined, and the rotational

motion of the molecule completely described.[9-13] This greatly facilitates the evaluation of models for the correlation times, which, of course, are proportional to the diffusion coefficients. These models have acquired increased sophistication (which, unfortunately, is usually accompanied by decreased practical utility, but this situation is improving). In addition to this, changes in the diffusion coefficients with varying experimental conditions, e. g., addition of other compounds, temperature, can be used to shed further light on relatively complex interactions in the liquid phase. The quadrupolar nuclei that are commonly used for these studies are deuterium, nitrogen-14, and chlorine-35. This work has been extended by other workers, who have used it to help separate the contributions from the different mechanisms responsible for relaxation of spin $\frac{1}{2}$ nuclei.[14-16] For example, if the diffusion coefficients can be determined using quadrupole relaxation times for a deuterium labeled compound, then the intramolecular dipolar contribution for the proton containing molecule can be calculated exactly, assuming that the correlation times are the same, and the contribution left over after the dipolar contribution is subtracted out can be attributed to other mechanisms, chiefly the spin-rotational interaction.

The determination of the spin-rotational relaxation rate and the associated correlation time has also been aided by the development of methods for the calculation of the spin-rotation coupling constants. These methods have in turn relied upon the use of equations, developed in the 1950's by Ramsey and co-workers, relating

the spin-rotation coupling constants to the paramagnetic part of the absolute chemical shielding tensor for a given nucleus, and to the chemical shielding anisotropy for the nucleus.[17, 18] These equations, coupled with the use of molecular beam and pure rotational microwave spectroscopy methods to measure the spin-rotation coupling constants for simple molecules in the gas phase, the use of modern digital computers and improved wavefunctions to calculate the diamagnetic part of the chemical shielding, and the use of nmr in the nematic crystal phase, and Fourier transform nmr in the solid phase to measure chemical shielding anisotropies for more complicated molecules, have made possible the accurate determination of spin-rotation coupling constants for many molecules.

The development of Fourier transform nmr spectroscopy has also permitted the measurement of relaxation rates for the chemically useful but low natural abundance spin $\frac{1}{2}$ nuclei, carbon-13 and nitrogen-15.[19] Although measurements for nitrogen-15 have only been made very recently,[20] and are somewhat superfluous because nitrogen-14 relaxation times are easier to measure and interpret, the study of carbon-13 relaxation rates has become very important.

4. Density Matrix Treatment -- Isotropic Rotation[21]

The BPP method of calculating the relaxation rate was outlined in Section 2 mainly to illustrate the concepts involved in relaxation. A more general, and therefore more useful, method for

calculating T_1 and T_2 is the density matrix treatment, a technique derived from quantum statistical mechanics. Several authors have treated density matrix theory and its application to magnetic resonance in detail, so we will give only the results. We start with a system with Hamiltonian $\mathcal{H}$, written as the sum of a large time independent term $\mathcal{H}_0$ (the Zeeman interaction), and a smaller time dependent perturbation $\mathcal{H}_1(t)$, and a wavefunction $\Psi(t)$ which we expand in a complete set of time independent orthonormal functions $\{u_n\}$ as

$$\Psi(t) = \sum_n c_n(t)\, u_n \tag{26}$$

The elements of the density matrix ρ_{mn} are defined as the ensemble average of the products of the coefficients $c_n(t)$

$$\rho_{mn} = \overline{c_m^*(t)\, c_n(t)} \tag{27}$$

The expectation value of any Hermitian operator $\hat{Q}$ can be shown to be the trace of the product of the matrix of $\hat{Q}$ and the density matrix

$$\overline{\langle \hat{Q} \rangle} = \mathrm{Tr}\{\underset{\frown}{\rho}\, \underset{\frown}{\hat{Q}}\} \tag{28}$$

The time evolution of this equation can be found using the time dependent Schrödinger equation, perturbation theory, and by a transformation to what is called the interaction representation defined by

$$\rho^I(t) = \exp(i\mathcal{H}_0 t/\hbar)\,\rho(t)\exp(-i\mathcal{H}_0 t/\hbar)$$
$$\mathcal{H}_1^I(t) = \exp(i\mathcal{H}_0 t/\hbar)\,\mathcal{H}_1(t)\exp(-i\mathcal{H}_0 t/\hbar) \tag{29}$$

The result is

$$\frac{d\overline{\langle \hat{\underset{\sim}{Q}} \rangle^I}}{dt} = \langle \hat{a} \rangle = -\,\mathrm{Tr}\{\hat{a}\,(\underset{\sim}{\rho}^I - \underset{\sim}{\rho}_0)\} \tag{30}$$

where $\underset{\sim}{\rho}_0$ is the unperturbed thermal equilibrium density matrix and the operator $\hat{a}$ is given by

$$\hat{a} = \int_0^\infty d\tau\, \overline{[\mathcal{H}_1^I(t)\,[\mathcal{H}_1^I(t-\tau),\,\hat{Q}\,]]} \tag{31}$$

Hamiltonians for spin-lattice relaxation interactions can usually be expanded in the laboratory or spaced-fixed frame of reference in the general form

$$\mathcal{H}_1(t) = \sum_q (-1)^q F^{(q)}(t)\,A^{(-q)} \tag{32}$$

where the $F^{(q)}$'s are random functions of time, their time dependence arising from molecular motion, and the $A^{(q)}$'s are operators acting on the variables of the system, usually spin operators. Transformation of this $\mathcal{H}_1(t)$ into the interaction representation, substitution into Eq. (31), and suitable manipulations give as a result

$$\hat{a} = -\tfrac{1}{2}\sum_q J_q(\omega)\,[A^{(-q)}\,[A^{(q)},\,\hat{Q}\,]] \tag{33}$$

where $J_q(\omega)$ is the spectral density of the autocorrelation function $G(\tau)$

$$J_q(\omega) = \int_0^\infty d\tau\, G_q(\tau) \exp(iq\omega_0\tau) \tag{34}$$

$$G_q(\tau) = F^{(q)}(\tau)\, F^{(q)*}(t+\tau) \tag{35}$$

To demonstrate the use of this formalism, we will calculate the intramolecular dipole-dipole relaxation rate. The Hamiltonian for the dipolar interaction between two spins $\vec{I}$ and $\vec{S}$, separated in space by a vector $\vec{r}$ is[4]

$$\mathcal{H}_1 = \hbar\gamma_I\gamma_S \left[\frac{\vec{I}\cdot\vec{S}}{r^3} - \frac{3(\vec{I}\cdot\vec{r})(\vec{S}\cdot\vec{r})}{r^5} \right] \tag{36}$$

If we expand the vector dot products in terms of their x, y, and z components, transform from cartesian coordinates to polar coordinates, rewrite the operators I_x, I_y, S_x, and S_y in terms of the raising and lowering operators $I_\pm$, $S_\pm$, and rearrange, we obtain

$$\mathcal{H}_1 = \frac{\gamma_I\gamma_S\hbar}{r^3} (A+B+C+D+E+F) \tag{37}$$

where

$$A = (1 - 3\cos^2\theta)\, I_Z S_Z$$

$$B = -\tfrac{1}{4}(1 - 3\cos^2\theta)(I_+ S_- + I_- S_+)$$

$$C = -\tfrac{3}{2}\sin\theta\cos\theta\exp(-i\varphi)(I_Z S_+ + I_+ S_Z)$$

$$D = -\tfrac{3}{2}\sin\theta\cos\theta\exp(i\varphi)(I_Z S_- + I_- S_Z)$$

$$E = -\tfrac{3}{4}\sin^2\theta\exp(-2i\varphi)\, I_+ S_+$$

$$F = -\tfrac{3}{4}\sin^2\theta\exp(2i\varphi)\, I_- S_-$$

From this, the division into $F^{(q)}$'s and $A^{(q)}$'s is obvious

$$\begin{aligned} F^{(0)} &= (1 - 3\,\mathrm{Cos}^2\theta)/r^3 \\ F^{(\pm 1)} &= \mathrm{Sin}\,\theta\,\mathrm{Cos}\,\theta\,\exp(\mp i\varphi)/r^3 \\ F^{(\pm 2)} &= \mathrm{Sin}^2\theta\,\exp(\mp 2i\varphi)/r^3 \end{aligned} \tag{38}$$

$$\begin{aligned} A^{(0)} &= \alpha\,[-2/3\,I_Z S_Z + 1/6\,(I_+ S_- + I_- S_+)] \\ A^{(\pm 1)} &= \alpha\,[I_Z S_\pm + I_\pm S_Z] \\ A^{(\pm 2)} &= \alpha\, I_\pm S_\pm /2 \end{aligned} \tag{39}$$

where $\alpha = -3/2\,\gamma_I\,\gamma_S\,\hbar$. To find $1/T_1$ we want the time dependence of the expectation value of the operator I_Z, which, of course, is proportional to M_Z. So we let $\hat{Q} = I_Z$ in Eq. (33), use the $A^{(q)}$'s and $F^{(q)}$'s defined in Eq. (38) and (39) to find the commutators and spectral densities, substitute $\hat{\mathcal{A}}$ into Eq. (30), and try to reduce this to the form of the Bloch equation for longitudinal relaxation

$$d\langle I_Z\rangle/dt = -1/T_1\,(\langle I_Z\rangle - \langle I_Z\rangle_o) \tag{40}$$

If the spins $\vec{I}$ and $\vec{S}$ are like spins, then $\langle I_Z\rangle$ in Eq. (40) will be the sum of $\langle I_Z\rangle$ and $\langle S_Z\rangle$. However, if $\vec{I}$ and $\vec{S}$ are unlike, we will have separate equations for $\langle I_Z\rangle$ and $\langle S_Z\rangle$, which must be solved simultaneously. Here we will treat the case for like spins with $\hat{Q} = I_Z + S_Z$. From the standard angular momentum commutator relations, we can find

$$\left[A^{(0)}\left[A^{(0)}, I_z + S_z\right]\right] = 0 \tag{41}$$

$$\left[A^{(-1)}\left[A^{(1)}, I_z + S_z\right]\right] = 2\alpha^2 I_z^2 S_z + 2\alpha^2 I_z S_z^2 - \alpha^2 (I_- S_- + I_- S_+)(I_z + S_z)$$

$$\left[A^{(-2)}\left[A^{(2)}, I_z + S_z\right]\right] = \alpha^2 I_z (S_x^2 + S_y^2 + S_z) + \alpha^2 S_z (I_x^2 + I_y^2 + I_z)$$

Substituting these relations into Eq. (30) gives

$$\langle a_z \rangle = \tfrac{2}{3} \alpha^2 I(I+1) \langle I_z + S_z \rangle \left[J_1(\omega_I) + J_2(2\omega_I)\right] \tag{42}$$

which means that

$$1/T_1 = \tfrac{3}{2} \gamma^4 \hbar^2 I(I+1) \left[J_1(\omega_I) + J_2(2\omega_I)\right] \tag{43}$$

We must now calculate the spectral densities J_1 and J_2. To do this we must consider the rotational diffusion of the molecule, but first we want to rewrite the autocorrelation function $G(\tau)$ in terms of probability functions. Consider $y(t)$, a random function of time which has a probability $p(y, t)$ of having the value y at time t. The average value of y is $\overline{y(t)} = \int y\, p(y, t)\, dy$. Further, any function of y will be random and will have an average value $\overline{f(y)} = \int f(y)\, p(y, t)\, dy$. In order to calculate the correlation function we define a probability $p(y_1, t_1; y_2, t_2)$ that $y = y_1$ at t_1 and that $y = y_2$ at t_2. Associated with this is the conditional probability $P(y_1, t_1; t_2, t_2)$ that $y = y_2$ at t_2 given that $y = y_1$ at t_1. These two probabilities are related by

$$p(y_1, t_1; y_2, t_2) = P(y_1, t_1; y_2, t_2)\, p(y_1, t_1) \tag{44}$$

The autocorrelation function of f(y) is defined by

$$G(t_1, t_2) = \overline{f(t_1)\, f^*(t_2)}$$

$$= \int\int p(y_1, t_1; y_2, t_2)\, f(y_1)\, f^*(y_2)\, dy_1\, dy_2 \qquad (45)$$

$$= \int\int p(y_1, t_1)\, P(y_1, t_1; y_2, t_2)\, f(y_1)\, f^*(y_2)\, dy_1\, dy_2$$

For a stationary random function, $p(y, t)$ will be independent of time, and $p(y_1, t_1; y_2, t_2)$, $P(y_1, t_1; y_2, t_2)$, and $G(t_1, t_2)$ will depend only on the time difference $t_2 - t_1 = \tau$, so that

$$G(\tau) = \int\int p(y_1)\, P(y_1; y_2, \tau)\, f(y_1)\, f^*(y_2)\, dy_1\, dy_2 \qquad (46)$$

With $G(\tau)$ defined in this way, we will now discuss rotational diffusion. We wish to describe the motion of the dipole-dipole vector. The orientation of this vector with respect to the laboratory z direction is given by the polar angles θ and φ. $p(\Omega, t) = p(\theta, \varphi, t)$ is the probability of finding the vector with orientation Ω at time t. The autocorrelation function can be rewritten as

$$G(\tau) = \int\int p(\Omega_0)\, P(\Omega_0; \Omega, \tau)\, F^{(q)}(\Omega_0)\, F^{(q)*}(\Omega)\, d\Omega\, d\Omega_0 \qquad (47)$$

where the $F^{(q)}(\Omega)$ are given in Eq. (38). Debye[22] showed that the rotation of a vector contained in a rigid sphere of radius a moving in a medium of viscosity η can be described by the differential equation for diffusion over the surface of a sphere

$$1/D \frac{\partial p(\Omega, t)}{\partial t} = \nabla^2 p(\Omega, t)$$
$$= \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial p}{\partial\theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2 p}{\partial\varphi^2} \quad (48)$$

where D is the diffusion constant for rotational motion. In order to calculate the autocorrelation function we need the solution of this equation with the initial condition $p(\Omega_0, 0) = \delta(\Omega - \Omega_0)$, i.e., we want $P(\Omega_0; \Omega, \tau)$. The general solution of the diffusion equation is an expansion in a series of normalized spherical harmonics $Y_\ell^m(\Omega)$

$$p(\Omega, t) = \sum_{\ell, m} c_\ell^m(t) Y_\ell^m(\Omega) \quad (49)$$

Substituting this expansion into Eq. (48), and using the orthogonality of the Y_ℓ^m and also the relation $\nabla^2 Y_\ell^m(\Omega) = -\ell(\ell+1) Y_\ell^m(\Omega)$ we find

$$dc_\ell^m/dt = -D\ell(\ell+1) c_\ell^m \quad (50)$$

which can be solved to give

$$c_\ell^m(t) = c_\ell^m(0) \exp(-t/\tau_\ell) \quad (51)$$

where $\tau_\ell \equiv 1/\ell(\ell+1) D$. The delta function given the initial condition $p(\Omega_0, 0) = \delta(\Omega - \Omega_0)$ can also be expanded in spherical harmonics

$$p(\Omega_0, 0) = \delta(\Omega - \Omega_0) = \Sigma Y_\ell^{m*}(\Omega_0) Y_\ell^m(\Omega) \quad (52)$$

Since $p(\Omega, 0)$ is also given by $p(\Omega, 0) = \Sigma c_\ell^m(0) Y_\ell^m(\Omega)$, we have

$c_{\ell}^{m}(0) = Y_{\ell}^{m*}(\Omega_0)$, so that

$$P(\Omega_0 ; \Omega, t) = \Sigma\, Y_{\ell}^{m*}(\Omega_0)\, Y_{\ell}^{m}(\Omega) \exp(-t/\tau_{\ell}) \tag{53}$$

$p(\Omega_0)$, the probability that at $t = 0$ the dipolar vector was at orientation Ω_0 can be found by assuming that all orientations have equal probability. Therefore $p(\Omega_0)$ is equal to 1/unit surface area = $1/4\pi$ and

$$G(\tau) = \frac{1}{4\pi} \iint F^{(q)*}(\Omega) F^{(q)}(\Omega_0) \Sigma\, Y_{\ell}^{m*}(\Omega_0) Y_{\ell}^{m}(\Omega) \exp(-t/\tau_{\ell})\, d\Omega\, d\Omega_0 \tag{54}$$

Examination of the $F^{(q)}(\Omega)$ given in Eq. (38) shows that they can be related to the spherical harmonics of the second order ($\ell = 2$)

$$\begin{aligned} F^{(1)}(\Omega) &= \frac{1}{r^3} \sqrt{\frac{8\pi}{15}}\, Y_2^1(\Omega) \\ F^{(2)}(\Omega) &= \frac{1}{r^3} \sqrt{\frac{32\pi}{15}}\, Y_2^2(\Omega) \end{aligned} \tag{55}$$

When these are substituted into Eq. (54) and the orthogonality of the Y_{ℓ}^{m}'s is used, we obtain

$$G^{(1)}(\tau) = \frac{1}{r^6} \frac{2}{15} \exp(-|\tau|/\tau_2) \qquad G^{(2)}(\tau) = \frac{1}{r^6} \frac{8}{15} \exp(-|\tau|/\tau_2) \tag{56}$$

From Eq. (34), the spectral densities can be found to be

$$J_1(\omega_I) = \frac{2}{15} \frac{1}{r^6} \frac{2\tau_2}{1+\omega_I^2 \tau_2^2} \qquad J_2(2\omega_I) = \frac{8}{15} \frac{1}{r^6} \frac{2\tau_2}{1+4\omega_I^2 \tau_2^2} \tag{57}$$

and

$$1/T_1 = \tfrac{3}{2}\hbar^2\gamma^4 I(I+1)\,\frac{1}{r^6}\left[\frac{4}{15}\,\frac{\tau_2}{1+\omega_I^2\tau_2^2} + \frac{16}{15}\,\frac{\tau_2}{1+4\omega_I^2\tau_2^2}\right] \tag{58}$$

In the extreme narrowing limit where $\tau_2 \ll \omega_I$,

$$R_1^{da} = 1/T_1 = \frac{2\gamma^4\hbar^2}{r^6}\, I(I+1)\,\tau_2 \tag{59}$$

This, we should remember, is for a spherical molecule, so the motion can be described by a single correlation time. Also note that $\tau_2 = 1/\ell(\ell+1)\,D = 1/6\,D$.

5. Density Matrix Treatment -- Anisotropic Rotation[9, 10]

The most general form of the diffusion equation is one in which the diffusion constant D is replaced by a diffusion tensor $\underset{\sim}{D}$. In the limit of molecular reorientation by random, small angle steps, the Debye limit, the diffusion equation is

$$\partial p(\Omega, t)/\partial t = -\vec{L}\cdot\underset{\sim}{D}\cdot\vec{L}\; p(\Omega, t) \tag{60}$$

where $\vec{L}$ is the angular momentum operator for the molecule. If we transform the diffusion equation to the particular molecular coordinate system that diagonalizes the diffusion tensor, we then have

$$\partial p(\Omega, t)/\partial t = -\mathcal{K}\, p(\Omega, t) \tag{61}$$

where $\mathcal{H} = \sum_i D_i L_i^2$, D_i is the diffusion coefficient for the i^{th} principal diffusion axis of the molecule, and L_i is the i^{th} Cartesian angular momentum operator. Comparison of $\mathcal{H}$ with the Hamiltonian for the quantum mechanical rigid rotor shows that with the substitution $D_i \rightarrow \hbar^2/2I_i$, the Hamiltonians are identical. I_i is the i^{th} principal component of the moment of inertia tensor. We therefore seek solutions of the diffusion equation which have the general form of an expansion in the stationary state free rotor eigenfunctions, which are well known and have been tabulated. As we did for isotropic diffusion, we want the conditional probability $P(\Omega_0 ; \Omega, t)$, subject to the initial condition $P(\Omega_0 ; \Omega, 0) = \delta(\Omega - \Omega_0)$. Also by analogy to the isotropic case, we can write

$$P(\Omega_0 ; \Omega, t) = \sum \Psi_n^* (\Omega_0) \Psi_n (\Omega) e^{-E_n t} \tag{62}$$

where the Ψ_n and E_n are the eigenfunctions and eigenvalues of $\mathcal{H}$.

The autocorrelation function is given by

$$G_{qq'}(t) = F^{(q)}(t) \; F^{(-q')*}(t + t') \tag{63}$$

The $F^{(q)}(t)$ above are those in the laboratory frame of reference. The $F^{(q)}$ are usually defined explicitly only in the molecular frame. If we assume that the $F^{(q)}$'s transform as second order spherical harmonics, then the transformation from the molecular to the laboratory frame can be done using the second order Wigner rotation matrices $R^{(2)}_{q,m}$ (23)

$$F^{(q)}(t) = \sum_{m} R^{(2)}_{q,m}{}^{*}(t)\ F'^{(m)}(0)$$
$$= \sum_{m} R^{(2)}_{-q,-m}(t)\ (-1)^{q-m}\ F'^{(m)} \tag{64}$$

where the prime indicates the molecular frame of reference, the angles in $R^{(2)}_{q,m}$ are referenced to the laboratory frame, and where, as indicated, the rotation matrices contain all of the time dependence. Because of this,

$$G_{qq'} = \sum_{m,m} (-1)^{q-q'-m-m'} F'^{(m)} F'^{(m')} \overline{R^{(2)}_{-q,-m}(t)\ R^{(2)*}_{q',-m'}(t+t')} \tag{65}$$

The ensemble average, as in the isotropic case, can be written in terms of the angular probability functions $p(\Omega_0)$ and $P(\Omega_0 ; \Omega, t)$

$$\overline{R^{(2)}_{-q,-m}(t)\ R^{(2)*}_{q',-m'}} = \iint R^{(2)}_{-q-m}(\Omega_0)\ R^{(2)*}_{q'-m'}(\Omega)\ p(\Omega_0)\ P(\Omega_0;\Omega, t)\, d\Omega\, d\Omega_0 \tag{66}$$

$p(\Omega_0)$ is again the probability that the molecular axes are aligned at Ω_0 at $t = 0$, only in this treatment it is a volume probability instead of a surface probability, so its value is the inverse of the unit volume in angle space, $8\pi^2$.

In Eq. (62) we expanded the conditional probability $P(\Omega_0 ; \Omega, t)$ in the asymmetric top rigid rotor wavefunctions Ψ_n. These wavefunctions can in turn be expanded in the symmetric top rigid rotor wavefunctions $\varphi^{J}_{K,M}$.

$$\Psi^{J}_{\tau,M}(\Omega) = \sum_{K} a^{J}_{K}(\tau)\ \varphi^{J}_{K,M} \tag{67}$$

where the a_K^J's are known and have been tabulated.[10] The sum is over K only, since J and M are still good quantum numbers for the asymmetric rotor. The expansion coefficients do not depend on M, since the wavefunctions are degenerate in M. We did this expansion because the symmetric rotor eigenfunctions can be written in terms of the Wigner rotation matrices

$$\varphi^J_{K,M}(\Omega) = (-1)^{M-K}\left[(2J+1)/8\pi^2\right]^{\frac{1}{2}} R^{(J)}_{-M,-K}(\Omega) \tag{68}$$

Since the $F^{(q)}(t)$ transform as second order spherical harmonics, only the $J = 2$ wavefunctions will be needed, because of the orthogonality of the rotation matrices. Substituting Eq. (68) into Eq. (67), Eq. (67) into Eq. (62), and Eq. (62) into Eq. (66), we find

$$\overline{R^{(2)}_{-q,-m}(t)\, R^{(2)}_{q',-m'}(t+t')} = \frac{(-1)^{-m-m'}\delta_{q,q'}}{5} \sum_\tau a^{(2)}_m(\tau)\, a^{(2)}_m(\tau)\, e^{-E^{(2)}_\tau t} \tag{69}$$

The delta function comes from the orthogonality of the rotation matrices. It eliminates cross-correlation terms and makes $G_{qq'}$ independent of q. Thus we have

$$G(t) = \frac{1}{5} \sum_{m,m'} F'(m)\, F'(m')^* \left[\sum_\tau a^{(2)}_m(\tau)\, a^{(2)}_{m'}(\tau) \exp\left(-E^{(2)}_\tau t\right)\right] \tag{70}$$

We now go from this general treatment to a specific case, that of quadrupole relaxation. Relaxation is due to the interaction of the quadrupole moment with the molecular electric field gradient at the nucleus. The interaction of the quadrupole moment with the

external static magnetic field orientates the nucleus in the laboratory frame of reference. The electric field gradient, which is due to the distribution of the electrons in the bonds of the atom containing the quadrupolar nucleus, fluctuates in orientation in the laboratory frame due to molecular rotation. As mentioned in Section 3, this mechanism will usually dominate to the exclusion of all others. The Hamiltonian for this interaction is[21]

$$\mathcal{H}_Q = \frac{e^2 q_Z Q}{4I(2I-1)} \left[3I_Z^2 - I^2 + \eta (I_+^2 + I_-^2)/2 \right] \tag{71}$$

where Q is the quadrupole moment, q_Z is the electric field gradient in the z direction of the coordinate system that diagonalizes the field gradient tensor, and η is the asymmetry parameter of the field gradient tensor. The quantity $e^2 q_Z Q$ is called the quadrupole coupling constant. It can be measured for a given molecule using pure rotational microwave spectroscopy in the gas phase, nuclear quadrupole resonance spectroscopy in crystalline solids, or nmr in liquid crystals.[24] From Eq. (71) we can define

$$F''(0) = \tfrac{1}{2} e^2 q_Z Q \qquad A^{(0)} = \frac{1}{2I(2I-1)} (3I_Z^2 - I^2)$$

$$F''(1) = 0 \qquad A^{(\pm 1)} = \frac{\sqrt{2}}{2I(2I-1)} (I_Z I_\pm + I_\pm I_Z) \tag{72}$$

$$F''(2) = \frac{\eta}{2\sqrt{6}} e^2 q_Z Q \qquad A^{(\pm 2)} = \frac{\sqrt{6}}{2I(2I-1)} I_\pm^2$$

The double prime on the $F^{(q)}$'s indicates that they are written in the coordinate system that diagonalizes the field gradient tensor. Since this coordinate system and that which diagonalizes the diffusion tensor will not, in general, be the same, we must again transform using the Wigner rotation matrices.

$$F'^{(m)} = \sum_{m'} R^{(2)}_{m,m'} F''^{(m')} \tag{73}$$

If we assume that $\eta \simeq 0$, which means there is cylindrical symmetry in the bonds of the atom containing the quadrupolar nucleus, which is an excellent approximation for single or triple bonds (e. g., deuterium), and a good approximation ($< 10\%$ difference in the relaxation rates) for other situations, then we can write

$$F'^{(m)} = \tfrac{1}{2} e^2 q_z Q \; R^{(2)*}_{m,o} \tag{74}$$

and also

$$G(t) = \frac{(e^2 q_z Q)^2}{20} \sum_{m,m'} R^{(2)*}_{m,o} R^{(2)}_{m',o} \sum_{\tau} a^{(2)}_{m}(\tau)\, a^{(2)}_{m'}(\tau) \exp(-E^{(2)}_{\tau} t) \tag{75}$$

The transformation between the prime coordinate system and the double prime molecular system can be described by two cylindrical angles θ and ϕ, so we can write

$$\begin{aligned} R^{(2)}_{0,0}(\theta,\phi) &= \tfrac{1}{2}(3\,\mathrm{Cos}^2\theta - 1) \\ R^{(2)}_{\pm 1,0}(\theta,\varphi) &= \mp\sqrt{\tfrac{3}{2}}\,\mathrm{Sin}\,\theta\,\mathrm{Cos}\,\theta\,\exp(\mp i\,\varphi) \\ R^{(2)}_{\pm 2,0}(\theta,\varphi) &= \sqrt{\tfrac{3}{8}}\,\mathrm{Sin}^2\theta\,\exp(\mp 2\,i\,\varphi) \end{aligned} \tag{76}$$

Substituting these expressions and the expansion coefficients $a_m^{(2)}(\tau)$ into Eq. (75) we obtain

$$G(t) = \frac{3(e^2 q_Z Q)^2}{80} \sum_{i=-2}^{2} c_i \exp(-t/\tau_i) \tag{77}$$

where $\tau_i = 1/E_i$, and the c_i and E_i are tabulated in Reference (10). From G(t) we can find the spectral density

$$J_q(\omega) = \frac{3(e^2 q_Z Q)^2}{80} \sum_{-2}^{2} c_i \frac{2\tau_i}{1+(q\omega\tau_i)^2} \tag{78}$$

and in the extreme narrowing limit

$$J(0) = \frac{3(e^2 q_Z Q)^2}{80} \sum c_i \tau_i \tag{79}$$

The rest of the procedure for calculating $1/T_1$ is the same as that for dipolar coupling for isotropic motion. The double commutators in Eq. (33) are calculated, and the expectation value found. The result is

$$\begin{aligned} R_1^Q = 1/T_1 &= \frac{3(2I+3)}{4I(2I-1)} J(0) \\ &= \frac{3}{40} \frac{(2I+3)}{I(2I-1)} (e^2 q_Z Q)^2 f(\Omega, D) \end{aligned} \tag{80}$$

where $f(\Omega, D)$ is a function dependent on molecular symmetry, the angles θ and φ, and the diffusion coefficients. We are principally

interested in $f(\Omega, D)$ for two special cases. One is the spherical rotor or the linear molecule, for which there is only one diffusion coefficient, so $f(\Omega, D) = 1/6\,D$, which is the isotropic result. The other is a symmetric rotor, for which we have two diffusion coefficients $D_{\|}$ and $D_{\perp}$, where the subscripts refer to axes parallel to and perpendicular to the symmetry axis of the molecule. In this case

$$f(\Omega, D) = \frac{\frac{1}{4}(3\,\mathrm{Cos}^2\theta - 1)^2}{6\,D_{\perp}} + \frac{3\,\mathrm{Sin}^2\theta\,\mathrm{Cos}^2\theta}{5\,D_{\perp} + D_{\|}} + \frac{3\,\mathrm{Sin}^4\theta}{4(2\,D_{\perp} + 4\,D_{\|})} \qquad (81)$$

where θ is the angle from the symmetry axis to the bond containing the nucleus of interest.

From this expression, we can readily see how the diffusion coefficients can be determined from the T_1 measurements for different quadrupolar nuclei in the molecule. For example, if a nucleus is on the symmetry axis ($\theta = 0°$), then $f(\Omega, D) = 1/6\,D_{\perp}$, so $D_{\perp}$ can be calculated from the relaxation rate. A T_1 measurement for any nucleus for which $\theta \neq 0°$ can then be used to calculate $D_{\|}$.

Other relaxation mechanisms, except for the spin-rotational interaction, have their $f(\Omega, D)$ the same as those for quadrupolar relaxation.[10]

6. Chemical Shielding and the Spin-Rotation Interaction

6.1. Chemical Shielding

In the first section we wrote the Zeeman Hamiltonian as

$\mathcal{H} = -\vec{\mu} \cdot \vec{H}_0$. But since the nucleus is shielded by the electrons surrounding it, we must consider not the static field $\vec{H}_0$, but the effective external field at the nucleus. This is written $\vec{H}_N = \vec{H}_0 - \underset{\sim}{\sigma} \cdot \vec{H}_0$, where $\underset{\sim}{\sigma}$ is called the chemical shielding or shift tensor. Expressions for the chemical shielding were first developed by Ramsey and co-workers,[17, 18] by starting with a classic mechanical expression for the magnetic field produced at the nucleus by the electron currents induced in the molecule by the external field, and then using quantum mechanical perturbation theory. The components of the shielding tensor for closed shell molecules is given by[17]

$$\sigma_{\nu\lambda} = \sigma^d + \sigma^p$$

$$= \frac{e^2}{2mc^2} \langle \Psi_0 \left| \sum_k \frac{\vec{r}_{ko} \circ \vec{r}_k \, \delta_{\nu\lambda} - (r_{ko})_\nu (r_k)_\lambda}{r_k^3} \right| \Psi_0 \rangle - \frac{2e}{mc} \langle \Psi_0 \left| \sum_k (\ell_k)_\nu / r_k^3 \right| \Psi_{1\lambda} \rangle \tag{82}$$

where ν and λ represent the x, y, and z directions in the molecule; the subscript k denotes the k^{th} electron of the molecule, so that $\vec{r}_k$ is the vector from the nucleus to the k^{th} electron; the subscript o in $\vec{r}_{ko}$ denotes that it is the vector from the origin of the magnetic vector potential to the k^{th} electron; Ψ_0 is the ground state electronic wavefunction of the molecule; $\Psi_{1\lambda}$ is the first order correction in the λ direction due to the perturbation of the external magnetic field -- usually called the "excited state" wavefunction; and ℓ_k is the orbital angular momentum operator for the k^{th} electron about

the nucleus. The two terms in the shielding σ^d and σ^p are called the diamagnetic and the paramagnetic shielding, respectively. The diamagnetic term, as indicated, involves only the zero order ground state wavefunctions. These wavefunctions can be approximated fairly well, so that σ^d can be calculated to a good degree of accuracy. The excited state wavefunctions Ψ_1, however, are much harder to get reasonable estimates for, so that calculation of this term is difficult. Fortunately, it has been shown that the paramagnetic shielding can be rewritten as the sum of two new terms, one of them a function of the spin-rotation coupling constants[18]

$$\sigma^p_{\lambda\lambda'} = -\frac{e^2}{2mc^2} \sum_{N'} \frac{[R^2_{NN'} - (R_{NN'})^2_\lambda] Z_{N'}}{R^3_{NN'}} + \frac{e^2}{4mc^2} \frac{h}{M g_N \mu_N^2} \Sigma C_{\lambda\lambda} I_\lambda \quad (83)$$

where the N' are the other nuclei in the molecule, $Z_{N'}$ is the charge of the N' nucleus, $R_{NN'}$ is the vector from nucleus N to nucleus N', m and M are the electron and proton masses, respectively, g_N is the nuclear g value, μ_N is the nuclear magneton, I_λ is the λ^{th} component of the moment of inertia in the molecular frame in which the moment of inertia tensor is diagonal (the principal inertial frame), and $C_{\lambda\lambda}$ is the spin-rotation coupling constant in the principal inertial frame. Spin-rotational coupling is coupling between the spin angular momentum of the nucleus and the magnetic field created by the rotation of the electrons and nuclei of the molecule. It will be dealt with in detail in Section 6.3.

6.2. Relaxation by Anisotropic Chemical Shielding[21, 25]

We describe here another relaxation mechanism which is related to the chemical shielding tensor, relaxation due to anisotropic chemical shielding. This occurs because anisotropy in the shielding tensor creates local magnetic fields at the nucleus, which are made time-dependent by the tumbling of the molecule in solution. The shielding tensor is always symmetric, and can thus be diagonalized in some molecular frame of reference. The diagonalized tensor, with principal values σ_x, σ_y, and σ_z, can be divided into an isotropic part $\sigma \vec{1}$, and an anisotropic part with zero trace and the principal values σ_x', σ_y', and σ_z', where $\sigma = 1/3\ (\sigma_x + \sigma_y + \sigma_z)$ and $\sigma_x' = \sigma_x - \sigma$, $\sigma_y' = \sigma_y - \sigma$, and $\sigma_z' = \sigma_z - \sigma$. The Hamiltonian is now $\mathcal{H}_z = -\gamma H_0\ (1 - \sigma)\ I_z + \gamma \vec{H}_0 \cdot \underset{\sim}{\sigma}' \cdot \vec{I}$. This division into two parts is useful since, in solution, only the average shielding σ can be measured. Furthermore, the first term, being isotropic, does not contribute to the relaxation, while the second term, being traceless, causes no net chemical shift, but does cause relaxation. It is convenient to write $\underset{\sim}{\sigma}'$ in terms of σ_z' and an anisotropy coefficient $\eta = (\sigma_x' - \sigma_y')/\sigma_z'$.

$$\underset{\sim}{\sigma}' = \begin{pmatrix} \sigma_x' & & \\ & \sigma_y' & \\ & & \sigma_z' \end{pmatrix} = \sigma_z' \begin{pmatrix} -\frac{1}{2}(1-\eta) & & \\ & -\frac{1}{2}(1+\eta) & \\ & & 1 \end{pmatrix} \qquad (84)$$

We wish to write $\mathcal{H}_\sigma = \gamma \vec{H}_0 \cdot \underset{\sim}{\sigma}' \cdot \vec{I}$ in the form $\mathcal{H} = \sum_m F^{(m)}(0)\ A^{(m)}$.

To do this, we expand $\mathcal{H}_\sigma$, and make the substitutions $H_\pm = H_x \pm i H_y$ and $I_\pm = I_x \pm i I_y$, and rearrange, which yields

$$\mathcal{H}_\sigma = \frac{\gamma \sigma'_z}{2} \left[3 H'_z I'_z - \vec{I}' \cdot \vec{H}' + \tfrac{1}{2} \eta (H_+ I_+ + H_- I_-)\right] \qquad (85)$$

so we can write

$$\begin{aligned} F^{(0)}(0) &= \frac{\gamma \sigma'_z}{2} & A^{(0)} &= 3 H_z I_z - \vec{I} \cdot \vec{H} \\ F^{(\pm 1)}(0) &= 0 & A^{(\pm 1)} &= \sqrt{\tfrac{6}{2}} (H_z I_\pm + I_z H_\pm) \\ F^{(\pm 2)}(0) &= \frac{\gamma \sigma'_z \eta}{2\sqrt{6}} & A^{(\pm 2)} &= \sqrt{\tfrac{6}{2}} H_\pm I_\pm \end{aligned} \qquad (86)$$

We can now follow the previously described procedure for calculating $1/T_1$ and find for extreme narrowing conditions

$$R_1^{csa} = 1/T_1 \quad \frac{8\pi^2}{15} \nu_0^2 (\Delta\sigma)^2 (1 + \eta^2/3) f(\Omega, D) \qquad (87)$$

where $\Delta\sigma = \sigma_z - \frac{1}{2}(\sigma_x + \sigma_y)$. An interesting feature of this mechanism is the fact that for extreme narrowing conditions $(1/T_2)/(1/T_1) = 7/6 \neq 1$.

6.3. Spin-Rotational Relaxation

BPP first suggested that the spin-rotation interaction might be important for nuclei in solution, but did nothing further than this.[4] Gutowsky and co-workers later showed that this mechanism is important for fluorine-19 relaxation in several freons (e.g.,

CHF_2Cl).[7] They attempted to describe the mechanism quantitatively by postulating a model in which the molecules are nearly stationary for relatively long periods of time, and then reorientate by random jumps of relatively short duration. The rotational magnetic field responsible for relaxation is on only during the jumps. A statistical analysis of this model, and calculation of the autocorrelation function gives a relaxation rate expression[7]

$$R_1^{sr} = \tfrac{1}{3}\gamma_I^2 \overline{H_{sr}^2} \Delta^2/\tau_c \qquad (88)$$

where Δ is the duration of the jump, $\overline{H_{sr}^2}$ is the mean squared magnitude of the magnetic field generated at the nucleus during the jump, and τ_c is the average time between jumps. This model correctly predicts the temperature dependence of the relaxation rate of fluorine-19 at higher temperatures for the freons studied (that is, T_1 decreases with increasing temperature). Eq. (88) also reduces to the equation that successfully describes the spin-rotation interaction in gases, if $\Delta = \tau_j$ = the time between transitions among the discrete rotational states that are found in the gas phase. However, $\overline{H_{sr}^2}$ and Δ were not evaluated quantitatively, so we cannot give a numerical prediction for R_1^{sr}.[7]

The Hamiltonian used for this work was $\mathcal{H}_{sr} = -\vec{\mu} \cdot \vec{H}_{sr} = -\hbar\gamma\vec{I} \cdot \vec{H}_{sr}$. To rewrite the Hamiltonian in terms of the spin-rotation coupling constants, we use the fact that the spin-rotational magnetic field is proportional to the molecular angular momentum vector $\vec{J}$, so that

$$\mathcal{H}_{sr} = -\hbar \vec{I} \cdot \underset{\sim}{C} \cdot \vec{J} \tag{89}$$

In the gas phase, where the rotation of the molecule is essentially free, $\vec{J}$ will be the angular momentum operator and will be quantized. However, in a liquid, the rotation is continuously interrupted, so that the rotational energy levels are blurred out by lifetime broadening, and J is no longer a valid quantum number. To oversome this difficulty, so that we can use the Hamiltonian in this form, we use the classical equipartition of energy, which states that every degree of freedom for a molecule has an average energy equal to $\frac{1}{2}$ kT. The rotational energy is $E_{rot} = \frac{1}{2} I\omega^2$. Since $I\vec{\omega} = \vec{J}\hbar$, $E_{rot} = \frac{\frac{1}{2}\overline{J^2}\hbar^2}{I} = \frac{1}{2}$ kT, so that $\overline{J^2} = IkT/\hbar^2$. Hubbard used this analysis, and a form of the density matrix theory called the semiclassical form of the density operator theory to calculate the spin-rotation contribution to the relaxation rate for spin $\frac{1}{2}$ nuclei in spherical top molecules[26]

$$R_1^{sr} = \frac{8\pi^2 IkT}{9\hbar^2}\left[\frac{(2C_\perp + C_\parallel)^2 \tau_1}{1+\omega_0^2\tau_1^2} + \frac{2(C_\perp - C_\parallel)^2 \tau_{12}}{1+\omega_0^2\tau_1^2}\right] \tag{90}$$

where I is the moment of inertia, $C_\parallel$ and $C_\perp$ are the parallel and perpendicular components of the spin-rotation coupling tensor, τ_1 is the angular velocity correlation time and τ_{12} is defined by $1/\tau_{12} = 1/\tau_1 + 1/\tau_2$. The derivation assumed that the orientation and the angular momentum of the molecule are not correlated, which will be approximately true if $\tau_1 \ll \tau_2$ or $\tau_2 \ll \tau_1$, i.e., the rates of fluctuation of the orientation and the angular momentum are greatly

different. For normal liquid systems, which are strongly interacting relative to gases, the molecule will undergo many changes in angular momentum before the orientation has changed appreciably, i.e., $\tau_1 \ll \tau_2$, Eq. (90) becomes

$$R_1^{sr} = \frac{8\pi^2 I kT}{3\hbar^2} \left(2C_\perp^2 + C_\parallel^2\right) \tau_1 \tag{91}$$

where we have also assumed extreme narrowing. If the molecule is not a spherical top, then the derivation referred to above must be modified. The easiest procedure is to assume that the spin-rotation coupling tensor can be diagonalized in the principal inertial frame of reference, and to neglect all cross-correlation terms in the autocorrelation function, i.e., the reorientation of the angular momentum about a given inertial axis is independent of the reorientation about the other two axes. Assuming this, and also that $\tau_1 \ll \tau_2$ and $\omega_0 \tau_1 \ll 1$, we find[27]

$$R_1^{sr} = \frac{8\pi^2 kT}{3\hbar^2} \sum_i C_{ii}^2 I_i \tau_{1i} \tag{92}$$

where the subscript i refers to the inertial coordinate system. For asymmetric molecules, the spin-rotation coupling tensor will not usually be symmetric, and so cannot be diagonalized, making Eq. (92) invalid. But since most of the molecules we will deal with here have an axis of symmetry, so that the coupling tensor can be diagonalized, we will not attempt to generalize further the expression

for R_1^{sr}.

We will consider, however, the effect of internal rotation on spin-rotation relaxation. A nucleus located on an internal rotor is coupled not only to the magnetic field created by the overall rotation of the molecule, but also to the field generated by the internal rotation of the top relative to the frame. For nuclei on a freely rotating top, this spin-internal-rotation interaction should be quite important, since the rotational magnetic field per unit angular momentum due to internal rotation will always be larger than that produced by the overall rotation of the molecule. We will consider only symmetric internal rotors, namely methyl and trifluoromethyl groups. When these groups are attached to a molecular frame which has at least two planes of symmetry (e. g., a benzene ring), the new spin-rotation Hamiltonian will be[28]

$$\mathcal{H}_{sr} = -\hbar \sum_k \vec{I}_k \cdot \underset{\sim}{C}(k) \cdot \vec{J} + C_\alpha (1 - I_\alpha/I_{aa}) \vec{I}_k \cdot \vec{j} \qquad (93)$$

where $\vec{I}_k$ is the nuclear spin angular momentum for the k^{th} spin, $\vec{J}$ is the total angular momentum of the molecule, $\vec{j}$ is the angular momentum of the top relative to the frame, C_α is the spin-internal-rotation coupling constant, and I_α and I_a are the moments of inertia of the top and the whole molecule about the top axis. In the limit of low barriers to rotation, it is useful to rewrite this in terms of the total angular momentum of the top $\vec{j}'$. We write $\vec{j}' = \vec{j}(1 - I_\alpha/I_a) + (I_\alpha/I_a) J_a$, or the total angular momentum of the top equals the

relative angular momentum of the top times the fraction of the inertia in the molecular frame plus the total angular momentum about the top axis times the fraction of the inertia in the top

$$\mathcal{H}_{sr} = -\hbar \sum_k \left[\vec{I}_k \cdot \underset{\sim}{C}(k) \cdot \vec{J} - C_\alpha (I_\alpha / I_a) I_{ka} J_a + C_\alpha \vec{I}_k \cdot \vec{j}' \right] \qquad (94)$$

Now it can easily be shown from classical electricity and magnetism that the spin-rotation magnetic field $\vec{H}_{sr} \cong \mu_0 / R^3 \vec{J}$, where μ_0 is the nuclear magneton. Since we have shown using the equipartition of energy that $\overline{J^2} = kT\, I/\hbar^2$, $\vec{H}_{sr}$ is proportional to $\sqrt{I}/R^3$. This indicates that the electrons and nuclei responsible for nearly all of the spin-rotation field will be those closest to the nuclei of interest, i.e., those located in the top itself. From these considerations, it can be seen that the two spin-rotation constants about the top axis, C_α and C_{aa} will be approximately in the ratio of the moments of inertia of the top and the whole molecule about this axis, i.e., $C_\alpha I_\alpha \simeq C_{aa} I_a$. Using this approximation in the expanded form of Eq. (94) gives[28]

$$\mathcal{H}_{sr} = -\hbar \sum_k \left[I_{kb} C_{bb}(k) J_b + I_{kc} C_{cc} J_c + I_{ka} C_\alpha j'_\alpha \right] \qquad (95)$$

If we further assume that $C_\alpha^2 \gg C_{bb}^2 \simeq C_{cc}^2$, because of the magnitudes of the respective moments of inertia, then the spin-lattice relaxation rate will be determined by the flucutations in $\vec{j}'$, so that we obtain Dubin and Chan's expression[28]

$$R_1^{sr} = \frac{8\pi^2 kT}{3\hbar^2} I_\alpha C_\alpha^2 \tau_{j'} \qquad (96)$$

where $\tau_{j'}$ is the correlation time associated with the fluctuations of j'. However, Burke has shown that this expression fails to predict the temperature dependence of the relaxation rate of the fluorines of benzotrifluoride, no matter what model for the correlation time is used.[29] In resolving this problem, Burke returned to the form of the Hamiltonian given in Eq. (93), which can be abbreviated $\mathcal{H}_{sr} = \mathcal{H}_J + \mathcal{H}_j$, where $\mathcal{H}_J$ is dependent only on the total angular momentum $\vec{J}$, and $\mathcal{H}_j$ is dependent on the relative internal angular momentum $\vec{j}$. Substituting this form of the Hamiltonian into the relaxation rate expression given in Section 2

$$1/T_1 \text{ oc } \int_{-\infty}^{\infty} \overline{\langle \beta | \mathcal{H}(t+\tau) | \alpha \rangle \langle \alpha | \mathcal{H}(t) | \beta \rangle} \; e^{-i\omega_{\beta\alpha}\tau} \qquad (22)$$

gives four terms, one each in $\overline{\mathcal{H}_J^2}$ and $\overline{\mathcal{H}_j^2}$, and two cross-correlation terms in $\overline{\mathcal{H}_J \mathcal{H}_j}$. Burke pointed out that there are two limiting cases in which the relaxation rate can be easily calculated, when the fluctuations of $\mathcal{H}_J$ and $\mathcal{H}_j$ are either completely correlated or completely uncorrelated.[29] The completely correlated limit is the one treated by Dubin, which gave Eq. (96). In the uncorrelated limit, the cross-correlation terms in the relaxation rate are zero, and there are two separate correlation times τ_J and τ_j. In the extreme narrowing limit

$$R_1^{sr} \text{ oc } \overline{\mathcal{H}_J(0)^2}\,\tau_J + \overline{\mathcal{H}_j(0)^2}\,\tau_j \tag{97}$$

$$= \frac{8\pi^2 kT}{9\hbar^2}(I_a + I_b + I_c)(C_{aa}^2 + C_{bb}^2 + C_{cc}^2)\,\tau_J + (1 - I_\alpha/I_a)\frac{8\pi^2 kT\, I_\alpha}{3\hbar^2} C_\alpha^2 \tau_j$$

This expression gives correctly the temperature dependence of $1/T_1$ for fluorine in benzotrifluoride.[29]

7. Correlation Times

Until now we have only discussed correlation times as they arise in the calculation of relaxation rates. Here we will go into detail about the attempts which have been made to calculate them accurately. Historically, the most important method for the study of correlation times has been dielectric relaxation. When an electric field is applied to a liquid whose molecules have permanent dipole moments $\vec{\mu}$, the molecules tend to line up with the field, producing a macroscopic polarization. When the field is removed, the polarization decreases with a time constant τ_M which is related to the time constant for molecular reorientation τ_μ by $\tau_M = F\,\tau_\mu$, where F is an internal field factor, and τ_μ characterizes the fluctuations in the angular orientation of the dipole moment vector. Debye derived a differential equation for the angular distribution function $f(\theta, t)$ for the dipole moments[22]

$$\xi \frac{\partial f}{\partial t} = \frac{1}{\text{Sin }\theta} \frac{\partial}{\partial \theta}\left[\text{Sin }\theta \left(kT \frac{\partial f}{\partial \theta} - M f\right)\right] \tag{98}$$

where θ is the angle between the field direction and the dipole moment, ξ is the rotational friction coefficient, and $M = \xi \, d\theta/dt$ is the torque exerted on a dipole moment which tends to turn it in the direction of the field. If we start at thermal equilibrium at $t = 0$, so that, from Boltzmann's law, $f = A \exp(\mu E_0 \cos \theta / kT)$, and then $E = 0$, so $M = 0$ for $t > 0$, we can obtain the solution

$$f(\theta, t) = A \left[1 + \frac{\mu E_0}{kT} \cos \theta \, \varphi(t)\right] \tag{99}$$

We find $\varphi(t)$ by substituting back into Eq. (98) (with $M = 0$), so that

$$f(\theta, t) = A \left[1 + \frac{\mu E_0}{kT} \cos \theta \exp(-2kTt/\xi)\right] \tag{100}$$

The time that it takes for the second term of this expression to fall to 1/e of its initial value, the relaxation time, is

$$\tau_\mu = \xi / 2kT \tag{101}$$

In a more modern treatment based on Debye's, we first consider a rotating dipole moment and then perform an ensemble average.[30] We also include a term for the free rotation of the molecule, which will be proportional to the moment of inertia I and the second time derivative of the angle θ. The equation of motion of a single dipole is

$$I \frac{d^2\theta}{dt^2} = -\xi \frac{d\theta}{dt} + M(t) \tag{102}$$

where $M(t)$ again represents the fluctuating torques. Multiplying

by θ and using the relations

$$\theta \frac{d^2\theta}{dt^2} = \frac{d(\theta\dot{\theta})}{dt} - (d\theta/dt)^2 \qquad \theta \frac{d\theta}{dt} = \frac{d(\tfrac{1}{2}\theta^2)}{dt} \tag{103}$$

we obtain

$$I \frac{d^2}{dt^2}(\tfrac{1}{2}\theta^2) + \xi \frac{d}{dt}(\tfrac{1}{2}\theta^2) = I(d\theta/dt)^2 + \theta M(t) \tag{104}$$

We now introduce the distribution function at thermal equilibrium f_0 and perform an ensemble average, denoted by $\overline{\qquad}$.

$$I \frac{d^2}{dt^2}\overline{(\tfrac{1}{2}\theta^2 f_0)} + \xi \frac{d}{dt}\overline{(\tfrac{1}{2}\theta^2 f_0)} = \overline{I\dot{\theta}^2 f_0} + \overline{\theta M(t) f_0} \tag{105}$$

$\overline{\tfrac{1}{2}\theta^2 f_0}$ is obviously the mean square angular displacement, and $\overline{I\dot{\theta}^2 f_0}$ is the average rotational kinetic energy. To solve this equation, we assume that the $\theta M(t)$ term will average to zero, and replace the average kinetic energy by kT. For the initial conditions $\theta(0) = d\theta(0)/dt = 0$, we find

$$\overline{\tfrac{1}{2} f_0 \theta^2} = \frac{2kT}{\xi}\left[t - \frac{I}{\xi}(1 - \exp(-\xi t/I))\right] \tag{106}$$

We can consider this solution in two limits, the Debye limit and the free rotation or inertial limit.[31] In the Debye limit when the friction coefficient ξ is large

$$\overline{\tfrac{1}{2} f_0 \theta^2} \cong 2kT\ t/\xi \tag{107}$$

The correlation time, the time per unit angular displacement, will be

$$\tau_\mu = \xi/2\,kT \tag{108}$$

the same as Eq. (101). In the inertial limit, where ξ is small

$$\overline{\tfrac{1}{2} f_0 \theta^2} \cong kT\, t^2/I \tag{109}$$

and[31]

$$\tau_\mu = (I/kT)^{\frac{1}{2}} .$$

For the case of the Debye limit, the problem is how to obtain an expression for the rotational friction coefficient ξ. The most widely used expression is that derived by Einstein based on Stokes' law of classical hydrodynamics, in which it is assumed that the polar molecules behave as macroscopic spheres of radius a imbedded in a fluid of viscosity η so that $\xi = 8\pi a^3 \eta$.[22]

We note that in treating the reorientation of a molecular dipole moment we have dealt with the angle θ and Sin θ and Cos θ. In nuclear magnetic dipolar relaxation, the angular functions are proportional to $\text{Cos}^2\theta$, $\text{Sin}^2\theta$, and Cos θ Sin θ, that is, the dipolar coupling is a tensor interaction, rather than a vector interaction. The correlation time for the reorientation of an ℓ-rank tensor was defined in Eq. (51)

$$\tau_\ell = 1/\ell\,(\ell+1)\,D = \xi/\ell\,(\ell+1)\,kT \tag{110}$$

so that for the nuclear magnetic dipolar interaction

$$\tau_2 = \tau_\mu/3 = 4\pi a^3 \eta/3kT \qquad (111)$$

which is valid in the Debye limit of reorientation by the small angle jumps of Brownian motion. In the inertial limit, it can be shown that $\tau_2 \cong \tau_\mu$.[32]

The Debye relations have been tested many times using dielectric and nmr relaxation data. And although good agreement has been found for liquid water and for solutions of large molecules, the values for τ_2 predicted by Eq. (111) for most liquids or solutions are generally about an order of magnitude too long.[33] More seriously, the temperature dependence predicted by Eq. (111) is not correct, although this occurs for a fewer number of cases. There have been many attempts to modify or correct the Debye expression for τ_2, in order to obtain better agreement with experiment, ranging from purely empirical corrections to those on a rigorous theoretical basis. There have also been attempts to completely redo the basic theory for molecular reorientation. The attempts to correct the Debye expression naturally center around the two quantities in Eq. (111) which are adjustable, the molecular radius a and the viscosity η. Perhaps the most successful of these has been the microviscosity model of Gierer and Wirtz.[34] They considered a spherical solute molecule of finite size, with radius a_2, surrounded by spherical layers of solvent molecules, each layer of thickness $2a_1$. If the solute molecule is rotating with angular velocity ω, each of the surrounding layers will acquire an angular velocity due to the friction

between the layers, the m^{th} layer having angular velocity ω_m. At thermal equilibrium, the total torque acting on the m^{th} layer must be zero, so that the resistive friction is equal to the torque created by the rotation of the layer. From this treatment, after suitable summation, comes a microviscosity factor f, which we multiply the friction coefficient by[34]

$$f = \left[6a_1/a_2 + (1 + a_1/a_2)^{-3}\right]^{-1} \tag{112}$$

For a pure liquid, where $a_1 = a_2$, $f \cong 1/6$.

Hill has pointed out that for relatively dilute solutions of polar molecules in nonpolar solvents, the viscosity of the liquid will be essentially determined by interactions among the far more numerous solvent molecules.[35] However, it is the interaction between the solute and the solvent molecules that will determine the correlation time for the solute molecules. Hill used a theory of viscosity developed by Andrade to derive expressions for this mutual viscosity. In Andrade's theory,[36] the molecules in a liquid are taken to be vibrating with frequency ν about equilibrium positions which change only slowly with time. Viscosity, the frictional resistance caused by the transfer of momentum between parts of the liquid moving at different velocities, is due to collisions between adjacent molecules, during which time the two molecules move as one. This approach leads to the equation[36]

$$\eta = 1/3 \; c\nu m/\sigma \tag{113}$$

where m is the molecular mass, c the probability of collision, and σ the intermolecular distance. From this we can find the viscosity for a mixture of solvent (subscripted 1) and solute (subscripted 2)[35]

$$\eta_m = X_1^2 \eta_1 \sigma_1/\sigma_m + X_2^2 \eta_2 \sigma_2/\sigma_m + 2 X_1 X_2 \eta_{12} \sigma_{12}/\sigma_m \qquad (114)$$

where η_1 and η_2 are pure liquid viscosities, the X_i's are mole fractions, and η_{12} is the mutual viscosity, given by

$$\eta_{12} = \tfrac{1}{2} c_{12} \frac{\nu_1 + \nu_2}{\sigma_{12}} \frac{m_1 m_2}{m_1 + m_2} \qquad (115)$$

From this a correlation time can be found

$$\tau_\mu = \frac{3}{kT} \frac{I_{12} I_2}{I_{12} + I_2} \frac{m_1 + m_2}{m_1 m_2} \eta_{12} \sigma_{12} \qquad (116)$$

where I_2 is the moment of inertia of the solute molecule, and I_{12} is the moment of inertia of the solvent molecule about the center of mass of the solute molecule upon collision. For a pure polar liquid this reduces to[35]

$$\tau_\mu = \frac{3 (3 - \sqrt{2})}{2 kT} \eta_2 \sigma_2 \left(\frac{I_2 I_{22}}{I_{22} + I_2} \frac{2}{m_2} \right)^2 \qquad (117)$$

The Hill theory has been shown to give better results than the Debye theory with the microviscosity factor included for systems of relatively simple organic molecules, particularly when the solvent and solute molecules have comparable radii.[37] The agreement between

the concentration dependence predicted by the Hill expressions and that observed experimentally is particularly good.[38] However, for pure liquids, and for cases where the η/T dependence of the correlation time does not hold, it is of limited usefulness.

Corrections to the molecular radius a are less easily justified theoretically than those of the viscosity. The useful method for calculating a is to assume that Avogadro's number (N_a) of hexagonal close-packed spheres occupy 74% of the molar volume

$$N_a \frac{4\pi}{3} a^3 = .74\, V_m = .74\, M_w/\rho$$
$$a^3 = .74 \frac{3}{4\pi} M_w/N_a\rho \tag{118}$$

where M_w is the molecular weight, and ρ is the density.[6] The justification for saying that the value calculated from Eq. (118) is too large (making τ too long), seems to be that because τ is often found to be proportional to η/T, it is better to adjust the radius. (Because of the temperature dependence of the density, the value of a calculated fron Eq. (118) will be temperature dependent. However, because the temperature dependence of the density is much less than that of the viscosity, the effect on τ is relatively small.) The correction to a is usually written[27]

$$a = \kappa^{\frac{1}{3}} r_o \qquad 0 \leq \kappa \leq 1 \tag{119}$$

where r_o is the calculated molecular radius. Values of κ have been calculated empirically, and have been found to vary with both solvent

and solute, although they seem to remain relatively constant for a given solute in a number of similar solvents, based on a limited amount of data. McClung and Kivelson have derived a theoretical expression for κ[27]

$$\kappa_{\alpha\alpha} = \frac{9}{4r_o} \frac{\int_0^\infty \overline{M_\alpha(0)\, M_\alpha(t)}\, dt}{\int_0^\infty \overline{M(0)\, M(t)}\, dt} \tag{120}$$

where α denotes the x, y, or z molecular axis, and M and M_α are the intermolecular torques on the solute and the α component of the solvent, respectively. However, this expression for κ cannot be calculated, so it doesn't mean very much.

There is another method, which has been used by some workers, for calculating a^3. This involves calculating, using covalent bond distances and angles, and the van der Waals radii of the atoms, the molecular radius along each of the three principal inertial axes, and finding a^3 from $a^3 = a_x a_y a_z$. In Table I, we compare a^3 calculated assuming close-packing with a^3 calculated from bond distances for a number of organic liquids. As can be seen, the close-packing a^3 are generally larger than the molecular a^3 by a factor of 1.1-1.2. Since calculated values for the rotational correlation time are generally larger than the experimental values, we obtain better agreement between calculated and experimental values if the molecular a^3 is used to calculate τ_2. It might be thought that the wide-spread use of the close-packing a^3's is due mostly to their

Table I. Values for the Molecular Radius Cubed (a^3) Calculated Using the Close-Packing Formula and Molecular Dimensions

Compound	M (g/mole)	ρ (g/cm^3)	a^3_{cp}	a^3_{md}	a^3_{cp}/a^3_{md}
CF_3CO_2H	114.03	1.535	21.8	17.2	1.26
$C_6H_5CH_3$	91.14	.862	31.0	25.3	1.23
CS_2	76.14	1.256	17.8	10.9	1.63
C_6H_6	78.11	.874	26.2	23.8	1.10
CH_3I	141.94	2.265	18.4	15.6	1.18
CH_3CN	41.05	.780	15.4	12.6	1.22
CH_3Br	94.95	1.732	16.1	14.3	1.13
$CHBr_3$	252.77	2.890	25.6	23.6	1.09
$CHCl_3$	119.39	1.498	23.4	19.8	1.18
CCl_4	153.82	1.584	28.5	25.1	1.13
CBr_4	331.67	3.42	28.4	30.8	.92
CH_3OH	32.04	.793	11.8	11.7	1.01
CH_3CHO	44.05	.783	16.5	14.0	1.18
CH_3CO_2H	60.05	1.049	16.8	14.4	1.17
CH_3CH_2OH	46.07	.789	17.1	15.5	1.10
$(CH_3)_2CO$	58.08	.785	21.7	18.8	1.15
$CH_3C{=}C{-}CH_3$	54.09	.686	23.1	19.2	1.21
CCl_3F	137.37	1.46	27.6	22.1	1.25
C_6H_5F	96.10	1.024	27.5	25.1	1.10
HCO_2H	46.03	1.215	11.1	8.6	1.30
C_6H_{12}	84.16	.774	31.9	34.7	.92

ease of calculation.

We showed that in the inertial limit, where the rotational friction coefficient is small, so that the reorientation is essentially dynamically coherent, the correlation time depends only on the moment of inertia and the temperature. Steele has calculated the spectral density for the inertial limit and has found the more exact expression[31]

$$\tau_2 = \tfrac{1}{2} (\pi I/3 kT)^{\frac{1}{2}} \tag{121}$$

There are several obvious cases where the Debye limit would intuitively be expected not to hold. These would be for small, highly symmetric molecules with small intermolecular forces, such as liquid methane, CF_4, or even benzene. However, it can usually be shown that the correlation time for a given molecule is never completely independent of the medium in which the molecule is put, given a wide enough range of conditions. For such cases it is obvious that some expression which takes in both limits is necessary. The inertial model will still be useful, however, for describing internal rotation and rotation about axes with low moments of inertia, as we will see.

As mentioned in Section 3, much less work has been done on the subject of the correlation time for the reorientation of the angular velocity τ_1. This is because τ_1 enters into the relaxation rate expressions only when the spin-rotational interaction is important, and since there are usually other relaxation mechanisms

competing with the spin-rotation interaction, the unambiguous determination of experimental values for τ_1 is very difficult. As shown above, Debye showed that the correlation time is related to the rotational friction coefficient by $\xi/6\,kT$. Hubbard[26] has shown that ξ can be related to the moment of inertia by $\xi = IB$, where B is a proportionality constant with units of sec^{-1}. In Section 4, we used the diffusion equation to find an expression for the conditional probability $P(\Omega_0; \Omega, t)$, which we substituted into the autocorrelation function for rotational reorientation. In an analogous manner, Hubbard used the Langevin equation for Brownian rotational motion, which contains a term in the constant B, to find an expression for the conditional probability for angular velocity $P(\omega_0; \omega, t)$ from which it can be seen that the correlation time for angular velocity is given by $\tau_1 = 1/B$. From this it is obvious that $\xi = I/\tau_1$, and[26]

$$\tau_1 = I/6\,kT\,\tau_2 \qquad (122)$$

This expression, usually called the Hubbard relation, is used almost exclusively when it is necessary to calculate τ_1, despite the fact that it only holds theoretically for the limit of reorientation by small angle steps by Brownian motion, i.e., when $\tau_1 \ll \tau_2$. This is because no one has derived an alternative expression that can be easily calculated.

A simple test, called the χ test, has been developed to determine the applicability of the Debye limit.[11, 39] χ is defined for a particular molecular axis, subscripted i, as the ratio of $\tau_2 = 1/6\,D$ to the correlation time for the reorientation of a molecule in the

gas phase at low pressure $\tau_F = 3/5\ (I/kT)^{\frac{1}{2}}$

$$\chi_i = \frac{\tau_{2i}}{\tau_{F_i}} = \frac{5}{18 D_i}\left(\frac{kT}{I_i}\right)^{\frac{1}{2}} \tag{123}$$

It has been shown that when χ_i is greater than five, the mean angle turned per molecular collision is less than five degrees, so that the diffusion limit expressions should be valid.[39]

8. Intermolecular Dipolar Relaxation

Dipole-dipole coupling can also occur between nuclear moments on adjacent molecules. The basic form of the relaxation rate expression is the same as that for intramolecular relaxation[21]

$$R_1^{dr} = 3/2\ \gamma^4 \hbar^2 I\ (I+1)\ \left[J_1(\omega_0) + J_2(2\omega_0)\right] \tag{124}$$

for like spins. However, this mechanism is different in that it depends primarily on the relative translation of the two molecules, so the spectral densities will be different. The procedure for calculating them is the same as that for intramolecular relaxation, but instead of using the diffusion equation for rotational motion, we use that for translational motion, and find[21]

$$J_1(\omega_0) + J_2(2\omega_0) = \frac{4\pi N}{45 a^3}\ \tau_t \tag{125}$$

where N is the number of spins I per unit volume, and τ_t is the

correlation time for translational reorientation, defined from the diffusion equation as

$$\tau_t = d^2/2\,D_t \tag{126}$$

where d is the distance of closest approach for the molecules and is usually taken to be equal to 2a, and D_t is the translational diffusion coefficient. D_t was found by Stokes to be[22]

$$D_t = kT/6\pi\, a\, \eta \tag{127}$$

If N is given by $N = n_I \rho N_a / M_w$, where n_I is the number of I spins per molecule, then

$$R_1^{dr} = \frac{6\pi^2 \hbar^2 \gamma^4 \eta}{5kT} \quad n_I \quad \frac{\rho N_a}{M_w} \tag{128}$$

for like spin $\frac{1}{2}$ nuclei. For the relaxation rate for a spin $\frac{1}{2}$ nucleus by an unlike spin S, we have[40]

$$R_1^{dr} = \frac{16\pi^2 \hbar^2 \gamma_I^2 \gamma_S^2 S(S+1)}{15\ kT} \quad n_S \quad \frac{\rho N_a}{M_w} \tag{129}$$

This derivation ignores the effect of rotation on the intermolecular relaxation rate. Hubbard has derived an expression for R_1^{dr} which includes a correction for rotational motion.[41] This is found to be small, and is usually neglected. Accurate proton intermolecular relaxation rates can be found experimentally by measuring the relaxation rate as a function of the concentration of the proton

containing molecule in its perdeuterated analogue, and extrapolating to infinite dilution to find the inter- and intramolecular contributions. By the use of this technique, it has been shown that Eqs. (128) and (129) accurately (± 10%, at worst) predict the intermolecular dipolar relaxation rate, so that these equations can be used in place of experimental measurements. (5)

II. THE APPLICATION OF THE THEORY TO FLUORINE-19 AND CARBON-13 RELAXATION

1. Trifluoroacetic Acid

1.1. Introduction

T. E. Burke has shown that, for the fluorine-19 nuclei in benzotrifluoride, Eq. (97) of Part I correctly predicts the relaxation rate from 242°K to 542°K.[29] This assumes that the CF_3 top acts as a free internal rotor, and that the rotational magnetic fields generated by the internal and overall rotation fluctuate independently. He also showed that because of the internal motion of the CF_3 top, the intramolecular dipole-dipole coupling contribution to the relaxation rate is less than 10% of the total rate at 242°K, and less than that at higher temperatures, and so could be neglected in his analysis.[29] The validity of his analysis has been supported by studies of the pressure dependence of the fluorine relaxation rate in benzotrifluoride.[70] As a further application of his work, we will consider the case of trifluoroacetic acid (TFAA) in H_2O and D_2O solutions at room temperature.

1.2. Experimental Procedure

The trifluoroacetic acid and the trifluoroacetic anhydride used were manufactured by Matheson, Coleman, and Bell Company. The trifluoroacetic acid was used without further purification. The trifluoroacetic anhydride was reacted with an equivalent amount of D_2O to produce CF_3COOD, which was used without further treatment.

The spin-lattice relaxation times were measured using the pulse technique described in Section 1, Part 1. Detailed descriptions of the spectrometer and the data acquisition system used can be found elsewhere.[42, 29] The spin-lattice relaxation rates for the fluorines in CF_3COOH in H_2O and CF_3COOD in D_2O are shown in Figure 3. The error bars were determined by repeating the T_1 measurements several times, and calculating an average deviation. The measurements were made at frequencies between 13 and 14 MHz at 22°C.

1.3. Calculation Summary and Discussion

Table II gives a summary of structural and other physical data, including bond lengths and angles determined by Karle and Brockway by electron diffraction,[43] and moments of inertia calculated from these data, which were used in the calculation of the various relaxation rates for trifluoroacetic acid. The intermolecular dipolar coupling contribution to the relaxation rate was calculated using Eqs. (128) and (129) of Part I for a fluorine-19 nucleus in pure CF_3COOH and CF_3COOD and for CF_3COOH at infinite dilution in H_2O. We obtained values of R_1^{dr} of 0.027 sec^{-1} for F-F coupling in CF_3COOD, 0.007 sec^{-1} for H-F coupling in CF_3COOH, and 0.059 sec^{-1} for F-H coupling for CF_3COOH at infinite dilution in H_2O. The experimental values, determined from Figure 3, are 0.040, 0.007, and 0.062 sec^{-1}, respectively, illustrating the general validity of Eqs. (128) and (129). The intramolecular dipolar coupling contribution for two like spin $\frac{1}{2}$

FIGURE 3

Relaxation Rate ($1/T_1$) vs. Mole Fraction CF_3COO^-

for CF_3COOD in D_2O

and CF_3COOH in H_2O

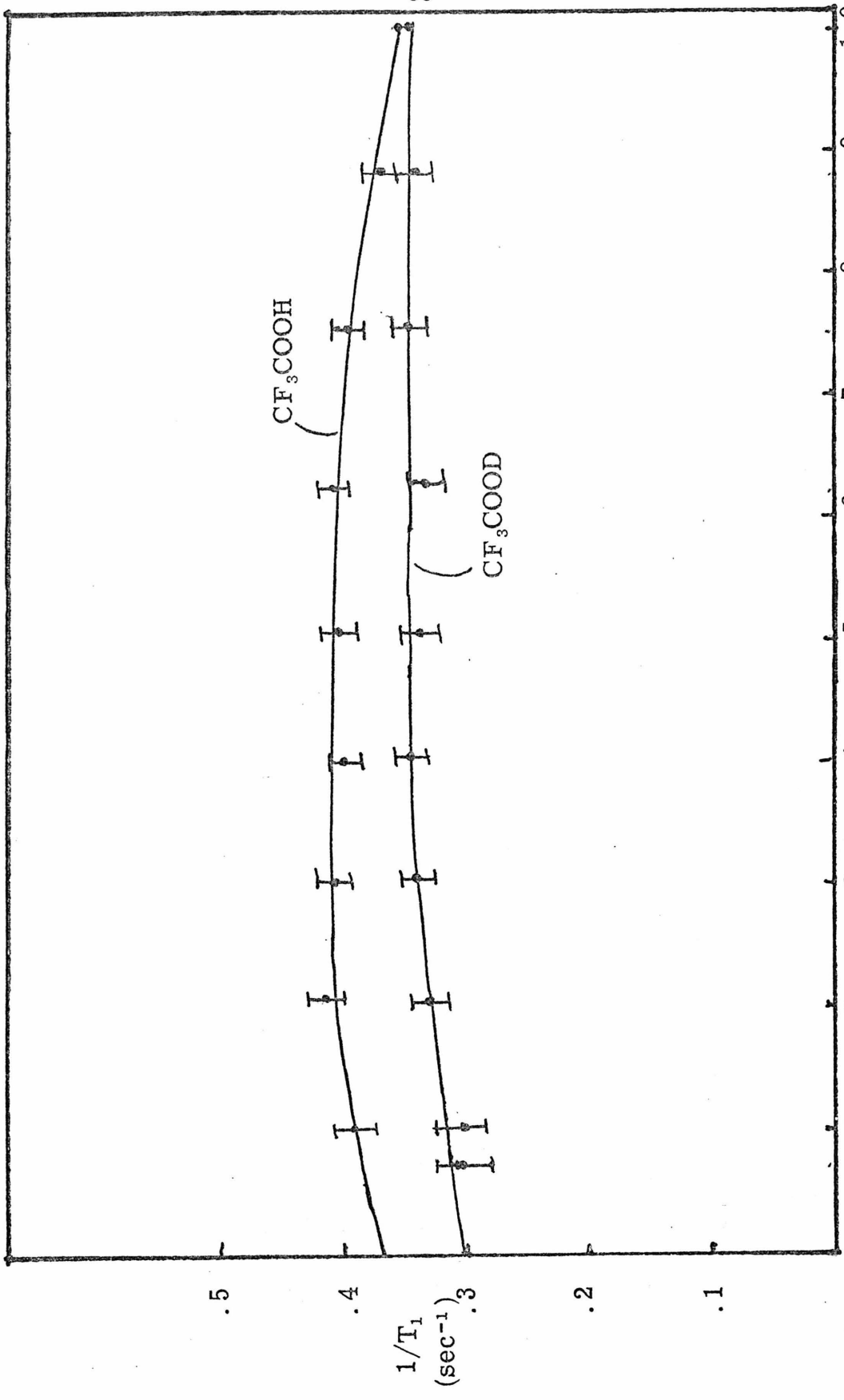

CF_3COOH
CF_3COOD
$1/T_1$ (sec^{-1})
.5
.4
.3
.2
.1
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
Mole Fraction $CF_3CO_2^-$

Table II. Parameters for CF_3COOH

Molecular weight	114.03 g/mole
Density (20°C)	1.491 g/cm^2
Viscosity (20°C)	.876 cp
Chemical shift	297. ppm
Molecular radius	$a^3 = 17.24\ A^3$
Bond lengths and angles	$r_{CF} = 1.36$ A
	$r_{CC} = 1.47$ A
	$r_{FF} = 2.22$ A
	$(r_{C-O} + R_{C=O})/2 = 1.30$ A
	$\angle$ FCF = 110° ± 4°
	$\angle$ OCO = 130° ± 3°
Moments of inertia (10^{-40} g-cm^2)	$I_{aa} = 230.$
	$I_{bb} = 370.$
	$I_{cc} = 405.$
	$I_{\alpha} = 148.$
Spin-rotation coupling constants (kHz)	$C_{aa} = -4.05$
	$C_{bb} = -2.11$
	$C_{cc} = -1.93$
	$C_{\alpha} = -6.30$

nuclei can be calculated from Eq. (59) of Part I

$$R_1^{da} = \frac{2\hbar^2 \gamma_I^4 I(I+1)}{r^6} \tau_2 \qquad (1)$$

For a molecule with more than two interacting spins, the treatment becomes more complicated, since linear combinations of the unperturbed spin eigenfunctions must be used for the coupled spin system. However, it can be shown that to a very good approximation, pairwise additivity of the interactions can be assumed,[44] such that

$$R_1^{da} = \frac{1}{n} \sum_{i<j} (R_1^{da})_{ij} \qquad (2)$$

where n is the number of interacting nuclei, i and j are spins, and the summation is over pairs of nuclei. The effect of interactions between dissimilar nuclei can be accounted for by adding to Eq. (2) additional pairwise interaction terms, each multiplied by a factor of 2/3 to correct for the decreased efficiency of the heteronuclear interactions.[21] We can write a general expression for the intramolecular dipolar relaxation rate for a spin I

$$R_1^{da} = \hbar^2 \gamma_I^2 \left[\frac{3}{2} \gamma_I^2 \sum_{I'} r_{II'}^{-6} + \frac{4}{3} \sum_S (S+1) \gamma_S^2 r_{IS}^{-6} \right] \tau_2 \qquad (3)$$

We must also consider the effect of the internal rotation on the intramolecular dipolar relaxation rate. Woessner has shown that for a nucleus on a freely rotating internal top, with correlation

times τ_2 for overall rotation and τ_2^{int} for internal rotation, an effective correlation time can be defined[45]

$$\tau_2^{eff} = \tfrac{3}{4}\left[\tfrac{1}{3}(3\,\mathrm{Cos}^2\theta - 1)^2\tau_2 + \mathrm{Sin}^2 2\theta\,\tau_2' + \mathrm{Sin}^4\theta\,\tau_2''\right] \qquad (4)$$

where the extreme narrowing limit has been assumed, θ is the angle between the spin-spin vector and the internal rotation axis, and $1/\tau_2' = 1/\tau_2^{int} + 1/\tau_2$, and $1/\tau_2'' = 4/\tau_2^{int} + 1/\tau_2$. This expression is equivalent to Eq. (81) of Part I, which describes the correlation time for a symmetric top molecule undergoing anisotropic rotational diffusion about its two axes. For the case of a CF_3 top, where the F-F vector is perpendicular to the internal rotation axis, Eq. (4) reduces to

$$\tau_2^{eff} = \tfrac{3}{4}\left[\tfrac{1}{3} + \frac{\tau_2^{int}}{\tau_2^{int} + 4\,\tau_2}\right]\tau_2 \qquad (5)$$

The limiting cases for the motion are $\tau_2^{int} \ll \tau_2$ (rapid internal motion) and $\tau_2^{int} \gg \tau_2$ (rigid molecule), which reduce τ_2^{eff} to $\tau_2/4$ and τ_2, respectively. From this we see that any internal motion in a molecule reduces the effectiveness of the intramolecular dipolar interaction. To calculate the internal rotation correlation time, we use Eq. (121), given in Section 7 of Part I for τ_2 in the inertial limit

$$\tau_2^{int} = \tfrac{1}{2}(\pi\, I_\alpha/3\,kT)^{\frac{1}{2}} = 3.1 \times 10^{-13}\ \mathrm{sec} \qquad (6)$$

We calculate τ_2 using the modified Debye model

$$\tau_2 = 4\pi a^3 \eta f/3\,kT = 2.61 \times 10^{-12}\ \mathrm{sec} \qquad (7)$$

where the microviscosity factor f is equal to 1/6 for pure TFAA, and a^3 is calculated from bond distances and Van der Waals radii. Using the above values, we find

$$\tau_2^{eff} = 0.272\ \tau_2 \text{ sec}$$

$$R_1^{da} = 0.0080 \text{ sec}^{-1}$$

So we see that, assuming free internal rotation for the CF_3 top, the relaxation rate is dominated by spin-rotation relaxation.

Before calculating the spin-rotation relaxation rate, we will outline the method used for the calculation of the spin-rotation coupling constants. In Section 6.1 we saw that the nuclear magnetic shielding constant can be related to the spin-rotation coupling constants. The average absolute shielding for a nucleus N can be written[18]

$$\sigma_N = \frac{e^2}{3mc^2}\left[\left\langle \Psi_0 \left| \sum_k r_{Nk}^{-1} \right| \Psi_0 \right\rangle - \sum_{N'} \frac{Z_{N'}}{R_{NN'}} + \frac{h}{4 M_{gN} \mu_N^2} \sum C_{ii} I_i \right] \tag{8}$$

where the symbols are defined as before. The sum of the first two terms is proportional to the total electrostatic potential at the nucleus N. For atoms like fluorine this potential is mostly determined by the core and non-bonded valence electrons, so that the molecular

environment of the atom is relatively unimportant for these terms. Using theoretical calculations of the diamagnetic shielding term and molecular beam measurements of the spin-rotation coupling constants for several fluorine containing molecules, Chan and Dubin[46] calculated a value of 470 ± 10 ppm (parts per million) for the sum of the first two terms in Eq. (8), or

$$\sigma_N = 470 \times 10^{-6} + (\sigma^{CI})_{av} \tag{9}$$

A similar expression can be written for the individual diagonal components of the shielding tensor, since Chan and Dubin also showed that, to a good approximation, the sum of the first two terms is isotropic, although the shielding will in general be anisotropic. Therefore we have

$$(\sigma_N)_{ii} = 470 + 0.2081\, C_{ii}\, I_i \tag{10}$$

where I_i is in units of 10^{-40} g-cm^2, C_{ii} is in kHz, and σ_N is in ppm. The absolute average chemical shielding constant (the chemical shift with respect to the bare fluorine nucleus) for TFAA is 197 ppm,[1] so that

$$(\sigma^{CI})_{ac} = -173 = \frac{.2081}{3} \sum_i C_{ii}\, I_i \tag{11}$$

If we denote the principal C-C axis of the TFAA molecule with the subscript a, and assume that to a good approximation for molecules with two planes of symmetry containing the principal axis we have

$$C_{bb} I_b \cong C_{cc} I_c \tag{12}$$

then

$$C_{aa} I_a + 2 C_{bb} I_b = -2494 \tag{13}$$

for TFAA.

The principal components of the chemical shielding tensor for the molecule CF_3H have been determined from studies of the anisotropy of the chemical shift when the molecule is trapped in a β-quinol clathrate.[47] If we transform these results into a coordinate system in which the inertial tensor is diagonal, we obtain for CF_3H[29]

$$(\sigma^{CI})_{xx} = -206 \text{ ppm} \qquad (\sigma^{CI})_{yy} = -113 \text{ ppm}$$
$$(\sigma^{CI})_{zz} = -194 \text{ ppm} \tag{14}$$

Since $I_z = 148 \times 10^{-40}$ g-cm^2, we have

$$(\sigma^{CI})_{\|} = (\sigma^{CI})_{zz} = -194 = .2081\, C_{\|}\, I_{\|}$$
$$C_{\|} = -6.30 \text{ kHz} \tag{15}$$

We can identify this value of $C_{\|}$ with C_{α} for molecules with a CF_3 top. And since we showed in Section 6.3 that, to a good approximation, $C_{aa} I_a \cong C_{\alpha} I_{\alpha}$, we can calculate

$$C_{aa} = -4.05 \text{ kHz}$$

and from Eq. (13) above find

$$C_{bb} = -2.11 \text{ kHz}$$

$$C_{cc} = -1.93 \text{ kHz}$$

for CF_3COOH. If we substitute these values, along with the moment of inertia values into Eq. (97) from Section 6.3

$$R_1^{sr} = \frac{8\pi^2 kT}{9\hbar^2} (I_a + I_b + I_c)(C_{aa}^2 + C_{bb}^2 + C_{cc}^2)\tau_J + (1 - I_\alpha/I_a)\frac{8\pi^2 kT}{3\hbar^2} I_\alpha C_\alpha^2 \tau_j \tag{16}$$

At 298°K

$$R_1^{sr} = 7.88 \times 10^{11} \tau_J + 2.01 \times 10^{11} \tau_j \tag{17}$$

From the value for τ_2 in Eq. (7) we can calculate τ_1 using the Hubbard relation, Eq. (122) from Section 7

$$\tau_1 = \bar{I}/6kT\ \tau_2 = 5.29 \times 10^{-14} \text{ sec} \tag{18}$$

where $\bar{I} = 1/3 (I_{aa} + I_{bb} + I_{cc})$.

In his treatment of benzotrifluoride and hexafluorobutyne-2, Burke[29] assumed that τ_J is proportional to τ_1

$$\tau_J = n_J \tau_1 = n_J \bar{I}/6kT\ \tau_2 \tag{19}$$

and that τ_j is proportional to τ_1 in the inertial limit

$$\tau_j = n_j' \, I_\alpha/kT \, \tau_2^{int} = n_j \, (I_\alpha/kT)^{\frac{1}{2}} \qquad (20)$$

where n_J and n_j are empirical constants. He obtained values for n_J and n_j by plotting Eq. (17), R_1^{sr} vs. τ_1 for benzotrifluoride and hexafluorobutyne-2 at infinite dilution in various non-polar solvents, as shown in Figure 4. He obtained a single straight line for both compounds, and calculated $n_j = 1.5$ and $n_J = 0.69$ and 0.53 for benzotrifluoride and hexafluorobutyne-2, respectively. The values for the slope and the intercept are 5.75×10^{11} and 0.26, respectively. If the datum point obtained in this work, CF_3COOD in D_2O at infinite dilution, is plotted, it is reasonably close to the straight line (see Figure 4). If it is assumed that the points for CF_3COOD in other solvents will also fall on this line, then we can use the values for the slope and intercept to calculate n_J and n_j for CF_3COOD, and find $n_J = 0.73$ and $n_j = 2.1$. Plugging these values into Eq. (17) we find

$$R_1^{sr} = 7.88 \times 10^{11} \, n_J \, \tau_1 + 2.01 \times 10^{11} \, n_j \, (I_\alpha/kT)^{\frac{1}{2}} \qquad (21)$$

$$= 0.030 + 0.260 \text{ sec}^{-1}$$

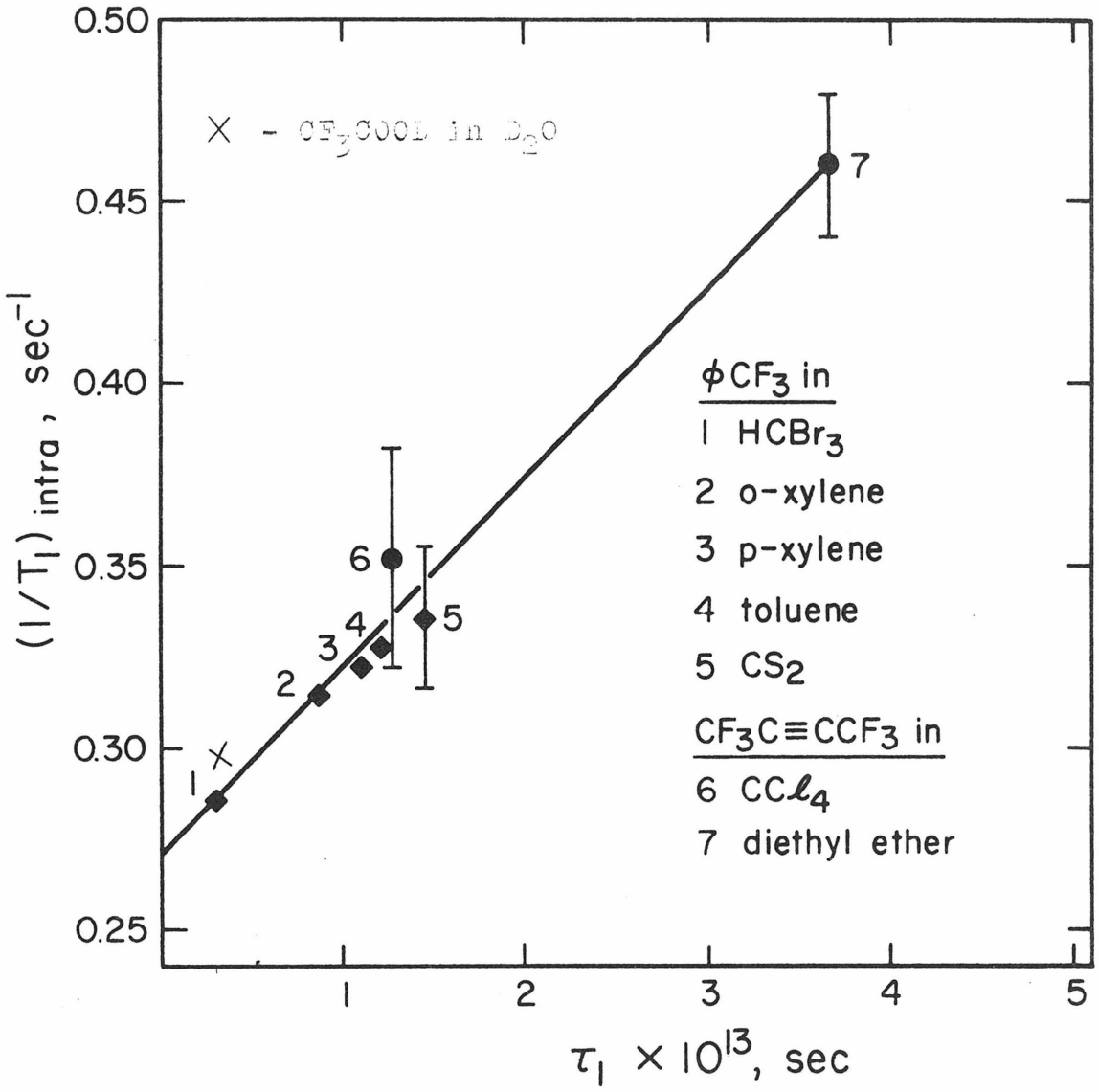
$$= 0.290 \text{ sec}^{-1}$$

Adding to this result $R_1^{da} = 0.008 \text{ sec}^{-1}$, we have $R_1 = 0.298 \text{ sec}^{-1}$, which is in very good agreement with the experimental value of 0.310 sec^{-1}. It should be noted that the major contribution ($\sim 90\%$) comes from the spin-internal-rotation term.

As can be seen in Figure 3, the relaxation rate of CF_3COOD

FIGURE 4

$(1/T_1)_{intra}$ vs. τ_1 for hexafluorobutyne-2 and benzotrifluoride.


0.50
0.45
0.40
0.35
0.30
0.25
$(1/T_1)_{intra}$, sec^{-1}
X - CF_3COOL in D_2O
ϕCF_3 in
1 $HCBr_3$
2 o-xylene
3 p-xylene
4 toluene
5 CS_2
$CF_3C\equiv CCF_3$ in
6 CCl_4
7 diethyl ether
1
2
3
4
5
6
7
1
2
3
4
5
$\tau_1 \times 10^{13}$, sec

changes very little as it is diluted in D_2O. The difference between the relaxation rate for pure CF_3COOD and that at infinite dilution can be accounted for by the loss of intermolecular F-F coupling with dilution. Studies of both Raman line broadening and proton chemical shifts[48] that occur when CF_3COOH is diluted in H_2O have shown that, above .50 mole fraction CF_3COOH, dissociation into CF_3COO^- and H is negligible. It has also been shown that CF_3COOH dimerizes readily, so there will also be a monomer-dimer equilibrium. From geometric considerations, the trifluoroacetate ion will have a six-fold barrier to rotation of the CF_3 top, so the rotation should be essentially free. The acid monomer, on the other hand, should have a three-fold barrier to rotation, of undetermined height, so it is possible that the rotation could be restricted. However, it has been shown using gas phase microwave spectroscopy to measure the hydrogen bond tunneling frequency of dimers such as CF_3COOH: CH_3COOH and CH_3COOH:HCOOH, that the protons in the hydrogen bonds of the dimers are exchanged very rapidly between the two oxygens, faster than the period for a rotation of the top could be, even for low barriers at room temperature.[49] Therefore, the barrier to rotation must be averaged for the two configurations of the molecule, which makes the oxygen atoms equivalent, and the barrier to rotation six-fold. From all this we can conclude that for the three species involved in the two equilibria

$$CF_3COOH \underset{}{\overset{K_{dissoc}}{\rightleftharpoons}} CF_3COO^- \; H$$

$$2\,CF_3COOH \underset{}{\overset{K_{dimer}}{\rightleftharpoons}} (CF_3COOH)_2$$

only the acid monomer could possibly have restricted rotation. Now, any restriction in the rotation of the CF_3 group would be expected to have relatively large effects on the relaxation rate, since the spin-internal-rotation coupling is by far the largest contributor to R_1, and free coherent rotation was assumed in deriving the relaxation rate expression. We can draw two possible conclusions from the fact that essentially no change occurs in R_1 as the CF_3COOD is diluted: (1) Since nothing is known about K_{dimer} in aqueous solution, nearly all of the undissociated acid might exist in the form of dimers, so that practically speaking only a dimer-dissociated ion equilibrium exists. (2) The monomer does not have a significant barrier to internal rotation. Of these two possibilities, the second seems more probable.

2. Toluene

Carbon-13, a spin $\frac{1}{2}$ nuclei, is an obvious choice for spin-lattice relaxation studies, simply because of the large number of carbon containing compounds and their importance to chemistry. Equally obvious, however, are the two reasons why studies such as those done for protons of fluorine were not carried out until very recently: (1) the low natural abundance of carbon-13 (1.1%), (2) the low sensitivity of carbon-13 nmr (1.6% of an equal number of protons

at constant field). However, with the development of fast Fourier transform nmr methods, the measurement of carbon-13 spin-lattice relaxation rates has become relatively simple. The first published values for carbon-13 T_1's were made by a group of Estonians, who used adiabatic fast passage methods instead of Fourier transform nmr.[50] Unfortunately, most of their measurements do not agree with those measured since then by Fourier transform nmr. The first Fourier transform nmr measurements were done by D. Jones and H. Sternlicht in 1969, although these values remain unpublished.[51] Since that time, a number of other studies have been done on simple carbon containing compounds. We will attempt to extend the methods of calculation developed for fluorine spin-lattice relaxation rates to carbon-13.

For the first of these studies, we chose a molecule similar to benzotrifluoride and trifluoroacetic acid, toluene, specifically the methyl carbon-13 of toluene. Because of the low barrier to internal rotation of the methyl top in toluene, it is expected that the spin-internal-rotation interaction will be important for both the protons and the carbon-13 of the methyl top. In fact, Burke and Chan[29] and Parker and Jonas[52] have shown its importance for the methyl protons. We will now examine the carbon-13 relaxation.

The physical and structural data necessary for the calculation of the various relaxation rates for toluene at 25°C are given in Table III. The intermolecular dipolar contribution to the relaxation rate is calculated using Eq. (129) of Part I to be

Table III. Parameters for Toluene

Molecular weight (g/mole)	92.13
Density (g/cc - 20°C)	.862
Viscosity (cp - 25°C)	.552
Chemical shift (δ_{CS_2} - ppm)	171.8
Molecular radius (a^3)	31.34 A^3
Bond lengths and angles	$r_{C_\alpha - C_1}$ = 1.51 A
	$r_{C_\alpha H}$ = 1.11 A
	r_{CC} = 1.397 A
	r_{CH} = 1.09 A
	∠ C-C-C = 120°
	∠ C-C-H = 120°
	∠ H-C_α = 109.5°
Moments of inertia (10^{-40} g-cm^2)	I_{aa} = 153.3
	I_{bb} = 340.2
	I_{cc} = 488.0
	I_α = 5.50
Spin-rotation coupling constants (kHz)	C_{aa} = -.607
	C_{bb} = -.446
	C_{cc} = -.311
	C_α = -16.9

$$R_1^{dr} = \frac{4\pi^2 \hbar^2 \gamma_H^2 \gamma_C^2 \eta}{5\,kT} n_H \frac{\rho N_a}{M_w}$$

$$= 1.72 \times 10^{-3}\ sec^{-1} \qquad (22)$$

This is a much smaller contribution than is typical for fluorine or protons, mostly because the gyromagnetic ratio for carbon-13 is about 1/4 of that for the proton. Furthermore, it might be thought that Eq. (22) will tend to over-estimate the intermolecular dipolar contribution, since, because of the physical shielding of the carbon-13 by the protons and/or other atoms, the protons of neighboring molecules cannot approach the carbon as closely as is assumed by Eq. (22). But this consideration is almost unimportant, since R_1^{dr} is only about three per cent of the total relaxation rate.

The calculation of the intramolecular dipolar contribution is also straightforward. The correlation times τ_2 and τ_2^{int} can be calculated from Eqs. (7) and (6)

$$\tau_2 = \frac{4\pi a^3 \eta f}{3\,kT} = 2.94 \times 10^{-12}\ sec \qquad (7)$$

$$\tau_2^{int} = \tfrac{1}{2}\left(\pi I_\alpha / 3\,kT\right)^{\frac{1}{2}} = 5.92 \times 10^{-14}\ sec \qquad (6)$$

τ_2^{eff} can be calculated by substituting these values into Eq. (4), with θ equal to 70.5°. We find

$$\tau_2^{eff} = 0.123\ \tau_2 = 3.51 \times 10^{-13}\ sec \qquad (4)$$

and we can see that the internal rotation reduces τ_2 by about a

factor of eight. We now calculate R_1^{da} to be

$$R_1^{da} = n_H \frac{\hbar^2 \gamma_c^2 \gamma_H^2}{r_{CH}^6} \tau_2^{eff} = 5.78 \times 10^{10} \tau_2^{eff} = .0203 \text{ sec}^{-1} \quad (23)$$

The intramolecular dipolar contribution due to coupling between the methyl carbon-13 and the ortho protons of the toluene ring may also be estimated using the same procedure. This gives a value for R_1^{da} of 9.02×10^{-5} sec^{-1}, which is negligible and will be neglected, along with the contributions from coupling with the other ring protons. The value obtained does serve to illustrate the point that, in general, because of the small value for γ_c and the r^{-6} factor, only spins directly bonded to the carbon-13 in question will be important in determining the relaxation rate. Carbon-13's attached only to zero spin atoms will, in the absence of the spin-rotation interaction, have very long relaxation times.

Before calculating the spin-rotation coupling contribution to the relaxation rate, we must first calculate the spin-rotation coupling constants. We again use Eq. (8) for the average absolute magnetic shielding. Ozier, Crapo, and Ramsey[53] used the calculations of Huo[54] on the ground state electronic properties of $^{13}C^{16}O$ to find for the diamagnetic shielding

$$\sigma_N^d = \frac{e^2}{3mc^2} \langle \Psi_0 | \sum_k r_{Nk}^{-1} | \Psi_0 \rangle = 328.4 \times 10^{-6} \quad (24)$$

We can also calculate

$$\frac{e^2}{3mc^2} \sum_{N'} \frac{Z_{N'}}{R_{NN'}} = -66.60 \times 10^{-6} \tag{25}$$

which gives a value of 261.8 ppm for the sum of the first two terms in the shielding, which, as for fluorine, we will assume to be constant for carbon-13 in any molecule, so that

$$\begin{aligned} \sigma_N &= 261.8 \times 10^{-6} + \frac{e^2 h}{mc^2 4Mg_N \mu_N^2} \left(\sum_i C_{ii} I_i\right)/3 \\ &= 261.8 + .7792 \left(\sum_i C_{ii} I_i\right)/3 \end{aligned} \tag{26}$$

where σ_N is in units of ppm, C_{ii} is in kHz, and I_i is in 10^{-40} g-cm^2. Ozier, Crapo, and Ramsey also used molecular beam magnetic resonance to measure a value of -32.59 kHz for the spin-rotation coupling constant in ^{13}CO.[53] Substituting this value into Eq. (26) gives a value for the average absolute shielding σ_N of 5 ppm. A common reference for carbon-13 chemical shifts is carbon disulfide. Since ^{13}CO is 11.5 ppm upfield from $^{13}CS_2$,[55] the absolute chemical shielding of $^{13}CS_2$ is -6.5 ppm. We can now use the chemical shift of methane (δ_{CS_2} = 195.8 ppm)[56] and its moment of inertia ($I = 5.33 \times 10^{-40}$ g-cm^2) to calculate C = -17.45 kHz for methane from Eq. (26). If we then correct this for the difference in the C-H bond length between methane (1.11 A) and the methyl group of toluene (1.09 A), we find a value for the spin-rotation coupling constant for

the methyl rotor in toluene of $C_\alpha = -16.9$ kHz. If we assume, as we did for benzotrifluoride and TFAA, that $C_\alpha I_\alpha \cong C_{aa} I_a$, then we can calculate $C_{aa} = -.607$ kHz. Further assuming that $C_{bb} I_b \cong C_{cc} I_c$, we can use the chemical shift of the methyl carbon of toluene ($\delta_{CS_2} = 171.8$ ppm)[57] to find $C_{bb} = -.466$ kHz and $C_{cc} = -.311$ kHz, again using Eq. (26).

We now calculate the spin-rotation relaxation rates

$$R_1^{sor} = \frac{8\pi^2 kT}{9\hbar^2} (I_a + I_b + I_c)(C_{aa}^2 + C_{bb}^2 + C_{cc}^2)\tau_J = 2.116 \times 10^{10}\, \tau_J \tag{27}$$

$$R_1^{sir} = (1 - I_\alpha/I_a)\frac{8\pi^2 kT}{3\hbar} I_\alpha C_\alpha \tau_j = 1.470 \times 10^{11}\, \tau_j \tag{28}$$

For the correlation time τ_J we again use the Hubbard relation

$$\tau_J = n_J \bar{I}/6\,kT\,\tau_2 = 4.51 \times 10^{-14}\ \text{sec} \tag{19}$$

where we have used $n_J = 1$. For the correlation time for the reorientation of the angular velocity of the top, we use

$$\tau_j = n_j (I_\alpha/kT)^{\frac{1}{2}} = n_j\, 1.16 \times 10^{-13}\ \text{sec} \tag{20}$$

Using these values we get

$$R_1^{sor} = 9.55 \times 10^{-4}\ \text{sec}^{-1}$$

$$R_1^{sir} = 0.0171\, n_j\ \text{sec}^{-1}$$

We see that the spin-overall-rotation interaction makes only a small contribution to the relaxation rate. The sum of R_1^{dr}, R_1^{da}, and R_1^{sor} is 0.0230 sec^{-1}. In Table IV we show the spin-internal-rotation contribution and the total relaxation rate and time for several values of n_j, since we cannot determine it empirically, as we could for CF_3 tops.

The experimental value at 25 °C for T_1 for the methyl carbon-13 of toluene is 16.5 ± .5 sec,[58] in good agreement with the value for $n_j = 2.0$. In fact, when $n_j = 2.2$, the calculated T_1 is equal to 16.5 sec. This value of n_j can be compared with $n_j = 2.1$ for TFAA and $n_j = 1.5$ for benzotrifluoride. It should also be noted that if the numerical factor $\frac{i}{2}\sqrt{\pi/3}$ is retained in τ_2^{int}, and τ_j is computed using $\tau_j = I_\alpha/kT\ \tau_2^{int}$, then $n_j = 1.95$. So it might be concluded that an empirical correction is not needed for τ_j, but that the difference between the experimental and the calculated values for T_1 is due to errors in other quantities. The most likely sources of error are in the value for τ_2, as discussed in Section 7 of Part I, and the value for the spin-rotation coupling constant.

We observe that the spin-internal-rotation interaction accounts for about 60% of the total relaxation rate at 25 °C, and most of the rest comes from intramolecular dipolar coupling. When we examine the temperature dependence of these two terms, we see that R_1^{sir} is proportional to the square root of the temperature, while R_1^{da} is proportional to η/T, so that R_1^{sir} will increase with temperature and R_1^{da} will decrease. Furthermore, since the viscosity of toluene

Table IV. Calculated Carbon-13 Spin-Lattice Relaxation Rates for the Methyl Carbon of Toluene

n_j	$R_1^{sir}(sec^{-1})$	$R_1^{tot}(sec^{-1})$	T_1 (sec)
1.0	.0171	.0401	25.0
1.5	.0257	.0487	20.6
2.0	.0342	.0572	17.5
2.2	.0376	.0606	16.5
2.5	.0428	.0658	15.2

exhibits the usual temperature dependence, $\eta = A \exp(E_a/RT)$, R_1^{da} decreases with temperature faster than R_1^{sir} increases. Above 0°C, the total calculated relaxation rate decreases rather slowly, from 0.0696 sec^{-1} at 0°C to .0605 sec^{-1} at 25°C (T_1 increases from 14.4 sec to 16.5 sec). Experimentally, values of T_1 between 16 and 18 sec are observed between 0° and 25°C, but this range of values seems to be the limit of error of the measurements, so the calculated numbers seem reasonable.

The calculated relaxation rate continues to decrease slowly up to the boiling point of toluene (110°C). This can be compared with the behavior of the fluorine relaxation rate for CF_3 tops, which increases at temperatures above room temperature because the spin-overall-rotation interaction becomes important. At 110°C the spin-overall-rotation contribution to the carbon-13 relaxation is still almost negligible.

Freeman and Hill have also measured the relaxation time for carbon-13 in the methyl group of toluene.[59] At 38°C, in an 80% toluene-20% C_6D_6 solution (the benzene provides a lock signal for their spectrometer), they found a T_1 of 15 ± 1 sec. Under these conditions we calculate a value of 17.2 sec for $n_j = 2.2$, which is reasonably good agreement. The discrepancy may be due to the presence of dissolved oxygen in their solution, since there is some doubt that their sample was totally degassed. Freeman and Hill have also measured the carbon-13 relaxation times for the various ring protons of toluene.[59] The values of T_1 are $>$ 50 sec, 22 ± 1

sec, 22 ± 1 sec, and 16 ± 1 sec for the quaternary, ortho, meta, and para carbons, respectively. As expected, the T_1 of the quaternary carbon is long. The fact that the T_1's of the other ring carbons are close to that of the methyl carbon may at first seem surprising, but this can be seen to reflect the rapid internal reorientation of the methyl top, and the important contribution from spin-internal-rotation coupling. For the ortho, meta, and para carbons, the dominant relaxation mechanism should be dipolar coupling between the carbon-13 and the proton attached to it. Calculation of this relaxation rate gives a T_1 of about 20 sec for the ring carbons, which is in essential agreement with the experimental rates. Although the methyl carbon-13 is coupled to three attached protons, the dipolar relaxation rate should be only about 3/8 of that for the ortho, meta, or para ring carbons, the factor of three arising from the three protons, and the factor of 1/8 from the shorter τ_2^{eff} when the methyl group can undergo fast internal reorientation. Therefore, were it not for the significant contribution from spin-internal-rotation coupling, the T_1 of the methyl carbon would be about 50 sec, a factor of three longer than the observed relaxation time.

Another molecule for which carbon-13 spin-rotation coupling constants have been measured is formaldehyde. Using the microwave absorption spectrum, Flygare and Weiss determined[60]

$$\left| 3/2\ C_{aa} + 3/4\ (C_{bb} + C_{cc}) \right| = 207.5 \pm 2.5 \text{ kHz} \qquad (29)$$

and also

$$C_{bb} - C_{cc} = 14.0 \pm 6.0 \text{ kHz}$$

They showed that C_{aa} should have a negative sign, and assumed that $|C_{aa}| > |C_{bb} + C_{cc}|$, in order to estimate C_{aa}. They then used the value for $C_{bb} + C_{cc}$ for oxygen-17 in formaldehyde to estimate $C_{bb} + C_{cc} = -7.0$ for carbon-13. This gives $C_{aa} = -135$ kHz, $C_{bb} = 3.5$ kHz, and $C_{cc} = -10.5$ kHz. From these values they calculated

$$\sigma_N^p = \frac{e^2}{3mc^2}\left[-\sum_{N'}\frac{Z_{N'}}{R_{NN'}}\frac{h}{4Mg_N\mu_N^2}\sum_i C_{ii}I_i\right]$$

$$= -79.0 \times 10^{-6} - 136. \times 10^{-6} \qquad (30)$$

$$= -215 \text{ ppm}$$

They then used a set of hybrid orbitals to calculate a value of 340 ppm for the diamagnetic part of the chemical shielding σ_N^d. This gives an average absolute shielding $\sigma_N = 125$ ppm. There is no reported value for the chemical shift of formaldehyde. However, using the values for acetone ($\delta_{CS_2} = -12.3$ ppm) and acetaldehyde ($\delta_{CS_2} = -6.8$ ppm),[61] we can estimate that for formaldehyde $\delta_{CS_2} \sim 3$ ppm. If the results for ^{13}CO are correct, then the absolute shielding for formaldehyde is -3.5 ppm, which is obviously inconsistent with Flygare and Weiss' result. We observe that for formaldehyde, the sum of the diamagnetic shielding and the first term in the paramagnetic shielding is 261.0 ppm. This is very close to our value of 261.8 ppm for ^{13}CO, which supports our assumption

that this sum is constant for carbon-13 in different molecules, and indicates that the discrepancy between the two results for the average shielding for formaldehyde comes entirely from the spin-rotation term in the shielding. If we replace Flygare and Weiss' estimate that $C_{bb} + C_{cc} = -7$ kHz with Eq. (26)

$$J_N(H_2{}^{13}CO) = -3.5 = 261.0 + .779\,(C_{ii}\,I_i)/3 \qquad (26)$$

We have, together with Eq. (29), three linear equations in C_{aa}, C_{bb}, and C_{cc}. These can be solved to give

$$C_{aa} = -124.9 \text{ kHz} \qquad C_{bb} = -6.4 \text{ kHz} \qquad C_{cc} = -20.4 \text{ kHz}$$

Thus we see that a change in the sum $C_{bb} + C_{cc}$ from -7 kHz to -26.8 kHz changes the spin-rotation term in the shielding from -136 ppm to -264.5 ppm, and the total average shielding from 125 ppm to -3.5 ppm, indicating the importance of a good estimate for $C_{bb} + C_{cc}$.

3. Carbon Disulfide

Since both of the predominant sulfur isotopes, sulfur-32 (95%) and sulfur-34 (4.2%), have zero nuclear spin, there can be no dipolar coupling for pure carbon disulfide. This leaves the spin-rotation and the anisotropic chemical shielding interactions as the only possible contributors to the relaxation rate. The chemical shielding anisotropy is expected to be relatively large for the

carbon-13 in CS_2, while the small size of this linear molecule and the absence of strong intermolecular forces make it probable that the spin-rotation interaction will be important. In 1956, McConnell and Holm proposed that the chemical shift anisotropy is the dominant mechanism, based on unstated experimental evidence that the relaxation time for $^{13}CS_2$ ($\sim$ 60 sec) is much shorter than that for CCl_4.[25] But this was before the spin-rotation mechanism was known to be important for liquids, and also before the measurement of the chemical shift anisotropy was possible, so their proposal could not be evaluated quantitatively. Nor was the obvious experiment done, that of investigating whether or not the relaxation rate is proportional to ω^2, as is predicted by the theoretical expression for the chemical shift anisotropy relaxation rate (Section 3.2 of Part I).

The chemical shift anisotropy mechanism has also been thought to be important for fluorine relaxation in several fluorocarbon compounds[62] (e.g., $CHFCl_2$), for which a frequency dependence of the relaxation rate was observed. But this dependence was later attributed to an increase in the sample temperatures at higher frequencies.[63] Furthermore, the relaxation rate of fluorine in UF_6, which has a very large chemical shift anisotropy (650 ppm), was shown to be independent of frequency from 2 to 56 MHz.[64]

For a linear molecule, the chemical shift anisotropy contribution to the spin-lattice relaxation rate at Larmor frequency ν_0 in the extreme narrowing limit is given by

$$R_1^{csa} = \frac{8\pi^2}{15} \nu_0^2 (\Delta\sigma)^2 \tau_2 \tag{31}$$

where $\Delta\sigma$ is the chemical shift anisotropy. The expression for the spin-rotation relaxation rate for a linear molecule is

$$R_1^{sr} = \frac{16\pi^2 kT}{3\hbar^2} C^2 I \tau_1 \tag{32}$$

The physical and structural data for carbon disulfide are given in Table V. The spin-rotation coupling constant for $^{13}CS_2$ can be calculated as outlined in Section 2, using Eq. (26)

$$\sigma_N = 261.8 + .519\, C\, I \tag{26}$$

The absolute chemical shielding was found in Section 2 to be - 6.5 ppm for $^{13}CS_2$. Using this value and the calculated value for the moment of inertia, we find C = - 2.0 kHz. We can also calculate the spin-rotation coupling constant from the measured value for the chemical shift anisotropy. Chan has shown that, to a good approximation, the traceless part of the shielding tensor in the principal inertial axis system can be found from the expressions[65]

$$\delta_a = \frac{e^2}{12mc^2} \frac{h}{Mg_N \mu_N^2} (2C_{aa}I_a - C_{bb}I_b - C_{cc}I_c) \tag{33}$$

$$\eta = \frac{\delta_b - \delta_c}{\delta_a} = \frac{3(C_{bb}I_b - C_{cc}I_c)}{(2C_{aa}I_a - C_{bb}I_b - C_{cc}I_c)} \tag{34}$$

Table V. Parameters for Carbon Disulfide

Molecular weight (g/mole)	76.14
Density (g/cc)	1.256
Viscosity (cp - 25°C)	.352
Chemical shift (δ_{CS_2} - ppm)	0.0
Molecular radius (a^3)	10.88 A^3
Bond length	r_{CS} = 1.558 A
Moment of inertia (10^{-40} g-cm^2)	258.46
Spin-rotation coupling constant (kHz)	-2.00

where δ_a is the chemical shift anisotropy, and η is the asymmetry parameter. For a linear molecule, $I_a = 0$, $I_b = I_c = I$, $C_{aa} = 0$, and $C_{bb} = C_{cc} = C$, so that $\eta = 0$ and

$$2/3\ (\Delta\sigma) = -.519\ C\ I \tag{35}$$

Pines, Rhim, and Waugh, using carbon-13 Fourier transform nmr in the solid state, measured a value for $\Delta\sigma$ of 425 ± 16 ppm.[66] Substituting this into Eq. (35), we find C = -2.11 ± .08 kHz, which is in good agreement with the value calculated above.

The calculation of the correlation times τ_2 and τ_1 is complicated by the fact that CS_2 is a small, highly anisotropic, nonpolar molecule. However, since it is a linear molecule, we need only describe the reorientation about the axis perpendicular to the internuclear axis. In calculating the rotational correlation time τ_2, we have used both the modified Debye and the modified Hill models. As discussed in Section 7 of Part I, the microviscosity factor of Gierer and Wirtz was introduced to modify the original Debye expression for τ_2 to account for the difference between solvent-solute interactions and those among solvent molecules. Their expression was

$$f = \left[6\,a_1/a_2 + (1 + a_1/a_2)^{-3}\right]^{-1} \tag{36}$$

where a_1 and a_2 are the solvent and solute radii, respectively. As we have seen, $f \cong 1/6$ for a pure liquid. However, Assink and Jonas have pointed out that the microviscosity factor can also be used to

account for the effects of anisotropic molecular shape.[67] For the i^{th} molecular axis we have

$$f_i = \left[6\, a/a_i + (1 + a/a_i)^{-3} \right]^{-1} \tag{37}$$

where a is the molecular radius and a_i is the radius about the i^{th} axis, calculated using bond lengths and Van der Waals radii r_w. For sulfur in CS_2, $r_w = 1.80$ A, so $r_\perp = 3.358$ A. Therefore $f_\perp = 0.239$ and

$$\tau_2 = \frac{4 \pi a^3 \eta f_\perp}{3\, kT} = 0.933 \times 10^{-12} \text{ sec}$$

$$\tau_1 = I/6\, kT\, \tau_2 = 11.2 \times 10^{-14} \text{ sec}$$

The Hill model for molecular reorientation, as modified for Assink and Jonas,[67] gives a molecular coefficient of friction for the i^{th} axis of a pure liquid as

$$\xi_i = \frac{12}{m_B} \eta_B \sigma_B \frac{I_{BB} I_i}{I_{BB} + I_i} \tag{38}$$

where σ_B is the molecular diameter ($\sigma_B = 2a = 4.43$ A), and I_{BB} is the moment of inertia of a second B molecule about the center of mass of a first B molecule ($I_{BB} = m_B \sigma_B^2$). Substituting for these and the other quantities, we find

$$\xi_\perp = 3.43 \times 10^{-25} \text{ erg-sec}$$

and consequently

$$\tau_2 = \xi_\perp / 6\,kT = 1.39 \times 10^{-12}\ \text{sec}$$

$$\tau_1 = I/6\,kT\,\tau_2 = I/\xi_\perp = 7.54 \times 10^{-14}\ \text{sec}$$

The results of the T_1 calculations at 25°C are given in Table VI. These results show, for the modified Debye model, that the chemical shift anisotropy is only 2.4% of the total relaxation rate at 25 MHz, but is 13.1% of the total rate at 62 MHz, so it is only at superconducting fields that the chemical shift anisotropy mechanism becomes important for carbon-13 disulfide. This conclusion disagrees with the measurements of Olivson, Lippmaa, and Past,[50] who obtained T_1 values of 30 sec at 15 MHz and 42 sec at 10 MHz, using adiabatic fast passage methods. At 25 MHz, the calculated value for the relaxation time using the modified Debye model (43 sec) is in good agreement with the value of 45 ± 1 sec measured by Jones and Sternlicht[51] at 25 MHz, with that of 45.5 sec measured by Spiess et al.,[68] at both 14 and 30 MHz, and with that of 48 sec measured by Shoup and Van der Hart[69] at 15 MHz. At 62 MHz, our value of 38.5 sec agrees well with the value of 36.8 sec measured by Spiess et al.

Spiess et al. have also used the measured values of the relaxation rate at temperatures from -106° to 35°C to calculate values for C and $\Delta\sigma$.[68] Their value for $\Delta\sigma$, 438 ± 44 ppm, is in good agreement with the measured value. However, they give

Table VI. Calculated Correlation Times and ^{13}C Spin-Lattice Relaxation Rates for CS_2 at 25°C.

Model	τ_2 $\times 10^{12}$ sec	τ_1 $\times 10^{14}$ sec	$1/T_1)_\sigma$ (sec^{-1})	$1/T_1)_{sr}$ (sec^{-1})	T_1 (sec)
Modified Hill	1.39	7.54	8.25×10^{-4} (a)	.0152	62.4
			5.07×10^{-3} (b)		49.4
Modified Debye	.933	11.2	5.55×10^{-4} (a)	.0226	43.2
			3.41×10^{-3} (b)		38.5

(a) ν_0 = 25 MHz

(b) ν_0 = 62 MHz

a value for C of - 13.8 kHz. The difference between this value and our calculated values of - 2.0 and - 2.11 kHz obviously needs an explanation. The expression they used for the calculation of C for a linear molecule is

$$\Delta\sigma = -\frac{e}{2mc}\,\frac{I}{g_N \mu_N}\,C \tag{39}$$

From Eq. (33) for δ_a, we find for a linear molecule

$$\delta_a = \frac{e^2 \hbar}{12 mc^2 M g_N \mu_N^2}\,(-2CI) = 2/3\,(\Delta\sigma) \tag{40}$$

Substituting in the theoretical expression for the nuclear magneton $\mu_N = e\hbar/2mc$, we have

$$\Delta\sigma = \frac{e}{2mcg_N \mu_N}\,2\pi CI$$

which is identical with Spiess' et al. expression, except for the factor of 2π. So the value for C reported should have been reported as - 13.8 kiloradians/sec instead of kHz. Dividing by 2π, we get C = - 2.2 kHz, in good agreement with the other values.

4. Benzene

From the three rather clear cut previous cases, we now proceed to one for which the results are more ambiguous, that of benzene, in the hope of seeing more clearly both the deficiencies and the

flexibility of the theory. We will also show proof of the assertions which were made about the relaxation of the ring protons of toluene in Section 2. Physical and structural data for benzene are given in Table VII. The viscosity and density are given at 13°C and 36°C, as well as at 25°C, because measurements of the carbon-13 spin-lattice relaxation time have been made at these temperatures. Benzene is a symmetric top molecule with a six-fold symmetry axis perpendicular to the plane of the ring. The subscript $\parallel$ denotes motion about the six-fold symmetry axis, and the subscript $\perp$ denotes the "flipping" motion of the ring about an axis in the plane of the ring. Note that $I_{\parallel} = 2 I_{\perp}$. $a_{\parallel}$ and $a_{\perp}$ are calculated from covalent and Van der Waals radii. The thickness of the benzene ring is generally given to be 3.5 A, so $a_{\parallel} = 1.75$ A. $a_{\perp}$ is found to be 3.69 A, so that $a^3 = 23.8$ A^3. Using this value and a microviscosity factor f = 1/6, and the Hubbard relation $\tau_2 \tau_1 = \bar{I}/6kT$, we calculate the τ_2 and τ_1 values given in Table VIII. The intermolecular dipolar relaxation rate can be calculated, as for toluene, from Eq. (22). The results are given in Table VIII.

The chemical shift of benzene relative to $^{13}CS_2$ is 65.0 ppm.[57] Substituting this value into Eq. (26), we get

$$C_{\parallel} I_{\parallel} + 2 C_{\perp} I_{\perp} = -782.86 \qquad (41)$$

The spin-rotation coupling constants $C_{\parallel}$ and $C_{\perp}$ cannot be uniquely determined from this equation. The usual procedure in cases such as this is to calculate an effective spin-rotation coupling constant

Table VII. Parameters for Benzene

Molecular weight (g/mole)	78.11
Density (g/cc) 13°C	.8862
25°C	.8734
36°C	.8616
Viscosity (cp) 13°C	.720
25°C	.604
36°C	.521
Chemical shift (δ_{CS_2}, ppm)	65.0
Molecular radius (a^3)	23.79 A^3
Moments of inertia (10^{-40} g-cm^2)	$I_{\|\|}$ = 295.42
	$I_{\perp}$ = 147.71
Spin-rotation coupling constants (kHz)	$C_{\|\|}$ = -.724
	$C_{\perp}$ = -1.144
Bond lengths and angles	r_{CC} = 1.397
	r_{CH} = 1.085
	∠ CCC = 120°
	∠ CCH = 120°

Table VIII. Calculated Correlation Times and Spin Lattice Relaxation Rates for Carbon-13 in Benzene Assuming Isotropic Motion

T°C	τ_2 ($\times 10^{12}$ sec)	τ_1 ($\times 10^{14}$ sec)	R_1^{dr} (sec^{-1})	R_1^{da} (sec^{-1})	R_1^{sr} (sec^{-1})	R_1 (sec^{-1})	T_1 (sec)
13	3.03	2.75	.00213	.0669	.00159	.0706	14.2
25	2.44	3.27	.00169	.0539	.00197	.0575	17.4
36	2.03	3.79	.00139	.0448	.00237	.0486	20.6

C_{eff} using

$$C_{eff} = \sum_i C_{ii} I_i / 3\bar{I} = -1.325 \text{ kHz} \qquad (42)$$

When substituted into the spin-rotation relaxation rate, Eq. (91) of Part I, this value gives a value for $\sum_i C_{ii}^2 = 3 C_{eff}^2 = 5.27 \times 10^6$. This procedure has been shown to be reasonably accurate for fluorine and phosphorus-31 in molecules that are spherical tops or roughly spherical tops. However, when the molecule is anisotropic, the accuracy decreases rapidly. Fortunately, the anisotropy of the carbon-13 shielding tensor has recently been determined to be $\Delta\sigma = 180$ ppm.[71] We thus have another equation for the spin-rotation coupling constants

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = \frac{e^2 \hbar}{4mc^2 g_N \mu_N^2} (C_{\parallel} I_{\parallel} - C_{\perp} I_{\perp}) \qquad (43)$$

$$180. = .7792 (C_{\parallel} I_{\parallel} - C_{\perp} I_{\perp})$$

These two equations, (43) and (41), can be solved to give

$$C_{\parallel} = -.724 \text{ kHz}$$

$$C_{\perp} = -1.144 \text{ kHz}$$

These values give $\sum_i C_{ii}^2 = 3.14 \times 10^6$, which leads to a 40% decrease in the spin-rotation relaxation rate, compared with that obtained when the effective spin-rotation coupling constant is used.

We can now finish our T_1 calculations

$$R_1^{da} = \frac{\hbar^2 \gamma_C^2 \gamma_H^2}{r_{CH}^6} \tau_2 = 2.208 \times 10^{10} \tau_2$$

$$R_1^{sr} = \frac{8\pi^2 kT}{3\hbar^2} \bar{I} (C_{\parallel}^2 + 2C_{\perp}^2) \tau_1 = 2.021 \times 10^8 T \tau_1$$

The results are given in Table VIII.

The calculated values for T_1 can be compared with experimental values of 23.0 ± 2 sec at 36°C, measured by Alger and Grant[72] using adiabatic fast passage, and 28 ± 1.5 sec at 13°C, measured by Jaeckle, Haberlen, and Schweitzer[58] using pulse techniques. It can be seen that, since the dominant relaxation mechanism, the intramolecular dipolar coupling, causes T_1 to decrease with decreasing temperature, the two experimental results are inconsistent with each other. However, the reasonably close agreement of our calculated value at 36°C with that of Alger and Grant does not necessarily imply that this value is correct, and the value at 13°C is not. In fact, adiabatic fast passage, the method used by Alger and Grant, has been generally found to give inconsistent results for other nuclei, unless experimental conditions and procedures are carefully controlled.

The intramolecular dipolar relaxation rate for protons in benzene has been measured by several groups by diluting C_6H_6 with C_6D_6. The values for T_1^{da} and the corresponding values for the rotational correlation time at 25°C are: T_1 = 60 sec, τ_2 = 2.4 ps (1 picosec = 10^{-12} sec) (Eisner and Mitchell,[73] 1961; Bonera and

Rigamonti,[74] 1965); T_1 = 103 sec, τ_2 = 1.4 ps (Powles and Figgins,[75] 1966); 1.7 ps (Bull and Jonas,[76] 1970). These can be seen to be somewhat lower than our calculated value of 2.44 ps. However, since the proton relaxation in benzene is dominated by intermolecular dipolar coupling (T_1^{dr} = 25 sec), the error in these values is quite large. An additional value for τ_2 in benzene has been determined by measuring the deuterium relaxation rate in C_6D_6[77] (τ_2 = 1.3 ps). Since the quadrupole relaxation completely determines the relaxation rate for deuterium in C_6D_6, it might be thought that the most accurate value for τ_2 would be 1.3×10^{-12} sec. If we, for the sake of argument, assume that this value is indeed correct, we can correct it for viscosity and temperature changes, and recalculate R_1^{da} at 13°C and 36°C. We find τ_2 = 1.61 ps at 13°C, and 1.08 ps at 36°C, which give R_1^{da} values of 0.0347 sec^{-1} (T_1 = 28.8 sec) at 13°C, and .0232 sec^{-1} (T_1 = 43.1 sec) at 36°C. This tends to support the T_1 value (28 sec) at 13°C measured by Jaeckle et al.[58] It is obvious that there can be no resolution of the discrepancies between the two measured values until the carbon-13 relaxation rate is redetermined for a range of temperatures. However, it should be emphasized that the correlation time results differ from each other at most by a factor of two, which, in the light of the basic difficulties which exist in the accurate measurement of relaxation rates, particularly for low natural abundance carbon 13, is not as bad a situation as the foregoing discussion might seem to imply.

With this in mind, we turn to another area which can be

related to relaxation rate studies, the nuclear Overhauser effect.[1, 78] The nuclear Overhauser effect (NOE) occurs when two spins I and S, of differing absorption frequencies, are coupled to one another by the dipole-dipole interaction. This is usually two unlike spins, such as carbon-13 and protons, which we will discuss here, but they can also be two like spins with different chemical shifts. When the S spins are saturated or "decoupled" (the spin energy level populations are made equal), by a strong rf field at the S absorption frequency, the coupling between the two spins produces a change in the spin energy level populations of the I spin. Since the intensity of the nmr absorption signal is proportional to the population difference between the spin energy levels, the decoupled absorption signal will differ from the coupled signal. For the case of carbon-13 coupled by the nuclear dipolar interaction to protons in the surrounding molecule(s), the transition probabilities are such that the carbon-13 absorption signal is enhanced by a factor of three (2.988, to be exact), when the protons are decoupled. However, if relaxation mechanisms other than the dipolar one are important for carbon-13 relaxation, then the NOE will be less than three. The formula for the NOE in terms of the relaxation rates which can be derived is[78]

$$\text{NOE} = 1 + \eta = 1 + \eta_{\max} (R_1^d/(R_1^d + R_1^o) \qquad (44)$$

where $\eta_{\max} = \gamma_H/2\gamma_C = 1.988$, R_1^d is the relaxation rate due to dipolar interactions, and R_1^o is the relaxation rate due to any other mechanisms. A measurement of the NOE can thus be used to

determine the presence of and to calculate the contribution of spin-lattice relaxation mechanisms such as the spin-rotation interaction. However, measurements of the NOE for carbon-13 are difficult to make, and even more difficult to reproduce, for several reasons. The fact that a ratio of intensities is used tends to magnify errors in the intensities. The low natural abundance of carbon-13 makes long time averaging a necessity, and time averaged intensities are often unreliable, because of changing spectrometer conditions. If Fourier transform nmr is used, unless the acquisition time is set longer than several T_1's, and other experimental factors are carefully controlled, the intensity measurements will be meaningless in terms of the actual signal intensities. Intensity measurements with long time averaging are further complicated by the fact that in the coupled spectrum, the carbon-13 resonances will usually be split because of spin-spin splitting caused by the protons. We mention in passing that because of the spin-spin splitting, carbon-13 relaxation times are usually measured with the protons decoupled. The fluctuating magnetic fields responsible for the spin-lattice relaxation are not changed by the saturation of the proton resonances, so T_1 is not affected by decoupling. The difficulty of rigid control of the sample temperature creates further problems in the measurement of the NOE. The relatively strong rf fields necessary for the decoupling of the protons, particularly when there is more than one species of proton present, tend to heat up the sample, so that vigorous cooling is necessary. In the usual experimental arrangement,

this creates an unstable situation, so that relatively large temperature fluctuations can occur, either rapidly or gradually. If, for example, the spin-rotation interaction is important for carbon-13 in a given molecule because the NOE depends on a ratio of relaxation rates, and because the temperature dependences of the spin-rotation and the dipolar relaxation rates are in the opposite direction, a small change in the temperature will produce a relatively large change in the NOE.

Alger and Grant measured a value of $1.80 \pm .15$ for η for benzene at 36°C.[72] They used this value to support their contention that carbon-13 relaxation is entirely due to intramolecular dipolar coupling, stating that the deviation from $\eta = 2.0$ (the theoretical limit, which they measured for cyclohexane) was not "statistically significant" for the experimental errors. Our calculations for benzene, if correct, show that the spin-rotation relaxation rate is about 7% of the total relaxation rate at 36°C, which is not a completely negligible contribution. We can also calculate a value for η of 1.89, which is in line with their experimental result. However, we will see below that a more realistic treatment of the motion of benzene casts further doubt on their assertion.

We have treated benzene as a spherical top, which, to a fair degree of approximation, it is. In the studies of the proton and deuterium relaxation times mentioned above, the reorientation of benzene has been assumed to be isotropic. However, in the solid state, it is known that benzene reorientates rapidly about its C_6 ($\parallel$)

axis, while there is little motion about the $C_2(\perp)$ axis.[79] In the liquid state, it is obvious from steric considerations, that there will be more hindrance to motion about the C_2 axis than the C_6 axis, since neighboring molecules do not have to move to allow rotation about the C_6 axis. This is opposite to what one would think if one merely considers the shape or the moments of inertia of the molecule.

We first attempt to correct for the anisotropy of benzene using Eq. (37) for the microviscosity factor about the i^{th} axis[67]

$$f_i = \left[6\, a/a_i + 1/(1 + a/a_i)^3\right]^{-1} \tag{37}$$

Using our values for $a_{\parallel}$ and $a_{\perp}$ of 1.75 A and 3.69 A, we find $f_{\perp}$ = .206 and $f_{\parallel}$ = .101. These give values for D_i at 25 °C of

$$D_{\perp} = kT/8\pi\, a^3 \eta\, f_{\perp} = 5.53 \times 10^{10}\ \text{sec}^{-1}$$

$$D_{\parallel} = 11.3 \times 10^{10}\ \text{sec}^{-1}$$

To find the effective rotational correlation time τ_2^{eff} for the combination of the two motions we use Eq. (81) of Part I

$$\tau_2^{eff} = f(\Omega, D) = \frac{\frac{1}{4}(3\,\text{Cos}^2\theta - 1)^2}{6\,D_{\perp}} + \frac{3\,\text{Sin}^2\theta\,\text{Cos}^2\theta}{5\,D_{\perp} + D_{\parallel}} + \frac{3\,\text{Sin}^4\theta}{2\,D_{\perp} + 4\,D_{\parallel}} \tag{45}$$

where θ is the angle between the symmetry axis and a C-H bond vector, so $\theta = 90^{\circ}$ and

$$\tau_2^{eff} = 1/24\ D_\perp + 3/4\ (2\,D_\perp + 4\,D_\parallel)$$
$$= 2.09 \times 10^{-12}\ \text{sec} \tag{46}$$

This value does not differ very much from the isotropic value for τ_2. But this is not too surprising, since the microviscosity factor corrects only for molecular shape, and not for the intermolecular forces that we have suggested are more important for benzene.

We now try a different approach. The rapid rotation about the C_6 ($\parallel$) axis in the solid state suggests that the correlation time about this axis might be more accurately described if the inertial model were used instead of the modified Debye model. We therefore calculate $\tau_{2\parallel}$ using

$$\tau_{2\parallel}^{int} = \tfrac{1}{2}\,(\pi\ I_\parallel / 6\,kT)^{\frac{1}{2}}$$
$$D_\parallel^{int} = 1/6\ \tau_{2\parallel} \tag{47}$$

but we still calculate $\tau_{2\perp}$ and $D_\perp$ using the microviscosity expressions. We calculate τ_{1i} using

$$\tau_{1i} = I_i / 6\,kT\ \tau_{2i} \tag{48}$$

and τ_2^{eff} using Eq. (46). The results are given in Table IX. We have also listed the results for R_1^{da} and R_1^{sr}, which were calculated using

$$R_1^{da} = n_H\ \frac{\hbar\ \gamma_C^2\ \gamma_H^2}{r_{CH}^6}\ \tau_2^{eff} \tag{23}$$

Table IX. Calculated Correlation Times and Spin-Lattice Relaxation Rates for Carbon-13 in Benzene Assuming Anisotropic Rotation

T°C	$\tau_{2\perp}$ $\times 10^{12}$ sec	$D_{\perp}$ $\times 10^{-10}$ sec^{-1}	$\tau_{2\parallel}$ $\times 10^{13}$ sec	$D_{\parallel}$ $\times 10^{-11}$ sec^{-1}	$\tau_{1\perp}$ $\times 10^{14}$ sec	$\tau_{1\parallel}$ $\times 10^{13}$ sec	τ_2^{eff} $\times 10^{12}$ sec
13	3.74	4.45	4.43	3.77	1.67	2.82	1.41
25	3.01	5.53	4.34	3.84	1.99	2.76	1.21
36	2.51	6.65	4.26	3.91	2.30	2.71	1.07

T°C	R_1^{dr} (sec^{-1})	R_1^{da} (sec^{-1})	R_1^{SR} (sec^{-1})	R_1 (sec^{-1})	T_1 (sec)	η
13	.00213	.0310	.00468	.0379	26.4	
25	.00169	.0267	.00491	.0333	30.1	1.70
36	.00139	.0236	.00514	.0301	33.2	1.65

$$R_1^{sr} = \frac{8\pi^2 kT}{3\hbar^2} \sum_i C_{ii}^2 I_i \tau_{1i} \qquad (49)$$

We see that τ_2^{eff} is now in good agreement with the experimental value determined from the deuterium relaxation time. We also notice that our calculated result for T_1 at 13°C, 26.4 sec, is in good agreement with the value of Jaeckle et al.[58] of 28 sec, but that at 36°C, 33.2 sec, does not agree well with that of Alger and Grant,[72] 23 sec. This supports our earlier remarks about the accuracy of the two measurements. Further, our calculated spin-rotation relaxation rate is now 17% of the total relaxation rate at 36°C, indicating that spin-rotation definitely cannot be neglected when considering benzene. If we recalculate η for the NOE using Eq. (44), we find $\eta = 1.65$, which differs significantly from the maximum value of 2.0, but which is still within the limits of error of the measurement of Alger and Grant, $1.80 \pm .15$. This indicates the care that must be taken in the interpretation of NOE results.

5. Acetonitrile and Methyl Iodide

Acetonitrile and methyl iodide are two molecules with obvious similarities in structure and size. Furthermore, although both molecules are not very far from being spherical if only the molecular radii along the molecular axes are considered, the concentration of mass along the symmetry axis means that the moments of inertia parallel to and perpendicular to the symmetry axis will differ by a factor of

about twenty for each molecule. It is expected, then, that the motion of these two molecules in solution will be highly anisotropic. Measurements of the spin-lattice relaxation rate for nitrogen-14 and deuterium in CD_3CN, and the use of these measurements to calculate $D_{\parallel}$ and $D_{\perp}$, the diffusion coefficients about and perpendicular to the symmetry axis, respectively, as was described in Section 5 of Part I, have shown that $D_{\parallel}/D_{\perp}$ is about ten at room temperature.[11, 80] Also, the values obtained for $D_{\parallel}$, from their magnitude and by use of the χ test, suggest that the Debye limit of small angle diffusion does not apply for motion about the symmetry axis, but that the inertial limit may hold. Indeed, it might be expected that the correlation times for angular and angular velocity reorientation about the symmetry axis will be essentially the same as those for the CH_3 top of toluene about the top axis. We will show below that this is the case.

Physical and structural data for methyl iodide and acetonitrile are given in Tables X and XI.

The chemical shift anisotropy of $^{13}CH_3I$ has been found to be -30.0 ± 3 ppm,[71] so we can find $C_{\parallel}$ and $C_{\perp}$ from

$$\sigma_N = 215.1 - 6.5 = 261.8 + .7792\,(C_{\parallel} I_{\parallel} + 2C_{\perp} I_{\perp})/3$$

$$\Delta\sigma = -30. = .7792\,(C_{\parallel} I_{\parallel} - C_{\perp} I_{\perp})$$

to be $C_{\parallel} = -17.1$ kHz and $C_{\perp} = -0.476$ kHz.

The chemical shift anisotropy for $^{13}CH_3CN$ has not been

Table X. Parameters for Methyl Iodide

Molecular weight (g/mole)	141.94
Density (g/cc) 25°C	2.279
30°C	2.265
35°C	2.252
Viscosity (cp) 25°C	.478
30°C	.459
35°C	.440
Chemical shift (δ_{CS_2}, ppm)	215.1
Molecular radius (a^3)	15.63 A^3
Bond lengths and angles	r_{CH} = 1.11 A
	r_{CI} = 2.139 A
	$\angle$ HCH = 111.4°
Moments of inertia (10^{-40} g-cm^2)	$I_{\parallel}$ = 5.50
	$I_{\perp}$ = 116.6
Spin-rotation coupling constants (kHz)	$C_{\parallel}$ = -17.08
	$C_{\perp}$ = -.478

Table XI. Parameters for Acetonitrile

Molecular weight (g/mole)	41.05
Density (g/cc) 25 °C	.7803
35 °C	.7695
Viscosity (cp) 25 °C	.345
35 °C	.319
Chemical shift (δ_{CS_2}, ppm)	193.0
Molecular radius (a^3)	15.43 A^3
Bond lengths and angles	$r_{CC} = 1.458$
	$r_{CN} = 1.157$
	$r_{CH} = 1.112$
	$\angle HCH = 109°16'$
	$\angle CCH = 109°40'$
Moments of inertia (10^{-40} g-cm^2)	$I_{\parallel} = 5.52$
	$I_{\perp} = 93.93$
Spin-rotation coupling constants (kHz)	$C_{\parallel} = -20.62$
	$C_{\perp} = -.938$

measured, but we expect that it will be similar to that for $^{13}CH_3I$. We assume a value of $\Delta\sigma = -20$ ppm, and calculate, using $\sigma_N = \delta_{CS_2} - 6.5 = 186.5$ ppm

$$C_{\parallel} = -20.6 \text{ kHz}$$

$$C_{\perp} = -0.938 \text{ kHz}$$

The correlation times for angular orientation and angular velocity for motion about the axes perpendicular to the symmetry axis have been calculated using the Debye limit microviscosity expressions

$$\tau_{2\perp} = \frac{4\pi a^3 \eta f_{\perp}}{3 kT} \qquad D_{\perp} = 1/6\ \tau_{2\perp} \tag{50}$$

$$\tau_{1\perp} = I_{\perp}/6 kT\ \tau_{2\perp} \tag{51}$$

where we have used $r_{\perp} = 2.84$ A to calculate $f_{\perp}$. We have calculated the correlation times about the symmetry axis using the inertial model

$$\tau_{2\parallel} = (\pi I_{\parallel}/3 kT)^{\frac{1}{2}} \qquad D_{\parallel} = 1/6\ \tau_{2\parallel} \tag{52}$$

$$\tau_{1\parallel} = n_j (I_{\parallel}/kT)^{\frac{1}{2}}$$

where we have used $n_j = 2.0$ in the calculation of $\tau_{1\parallel}$. The results for all the correlation times are given in Tables XII and XIII. Also listed are τ_2^{eff}, R_1^{da}, and R_1^{sr}, calculated from Eqs. (45), (23), and (49), respectively. We have also calculated η for the NOE using

Table XII. Calculated Correlation Times, Diffusion Constants and Relaxation Rates for Carbon-13 in Methyl Iodide

T°C	$\tau_{2\perp}$ $\times 10^{12}$sec	$D_\perp$ $\times 10^{-11}$sec^{-1}	$\tau_{2\parallel}$ $\times 10^{13}$sec	$D_\parallel$ $\times 10^{-12}$sec^{-1}	$\tau_{1\perp}$ $\times 10^{14}$sec	$\tau_{1\parallel}$ $\times 10^{13}$sec	τ_2^{eff} $\times 10^{13}$sec
25	1.33	1.25	1.18	1.41	3.55	2.31	4.00
30	1.26	1.33	1.17	1.42	3.70	2.29	3.82
35	1.19	1.41	1.16	1.43	3.86	2.28	3.69

T°C	R_1^{dr} (sec^{-1})	R_1^{da} (sec^{-1})	R_1^{sr} (sec^{-1})	R_1 (sec^{-1})	T_1 (sec)	η
25	.00095	.0231	.0363	.0604	16.6	.79
30	.00090	.0220	.0367	.0596	16.8	.77
35	.00084	.0213	.0370	.0591	16.9	.75

Table XIII. Calculated Correlation Times, Diffusion Constants and Relaxation Rates for Carbon-13 in Acetonitrile

T°C	$\tau_{2\perp}$ $\times 10^{12}$ sec	$D_{\perp}$ $\times 10^{-11}$ sec^{-1}	$\tau_{2\parallel}$ $\times 10^{13}$ sec	$D_{\parallel}$ $\times 10^{-12}$ sec^{-1}	$\tau_{1\perp}$ $\times 10^{14}$ sec	$\tau_{1\parallel}$ $\times 10^{13}$ sec	τ_2^{eff} $\times 10^{13}$ sec
25	1.07	1.57	1.19	1.41	3.57	2.32	3.54
35	.966	1.73	1.17	1.43	3.81	2.28	3.34

T °C	R_1^{dr} (sec^{-1})	R_1^{da} (sec^{-1})	R_1^{sr} (sec^{-1})	R_1 (sec^{-1})	T_1 (sec)	η
25	.00087	.0204	.0535	.0747	13.4	.57
35	.00070	.0193	.0544	.0744	13.4	.53

$\eta = 1.988\ R_1^d/R_1^{tot}$.

The calculated relaxation times can be compared with the following experimental values: for methyl iodide -- 11.1 ± .4 sec at 35°C (η = .42) by Lyerla, Grant, and Harris;[82] 13.4 sec at 25°C by Shoup and Van der Hart;[69] 23.8 ± .2 sec at 25°C (η = .42) by Jones and Sternlicht;[51] 13.4 ± .2 sec at 30°C (η = .52) by Farrar et al.;[83] 13.5 ± .4 sec at 26°C by Gillen, Schwartz, and Noggle;[84] for acetonitrile -- 13.1 ± 1.0 sec at 35°C (η = .53) by Lyerla, Grant, and Harris;[82] 21.5 ± .5 sec at 25°C (η = .52) by Jones and Sternlicht;[51] where we have listed in parentheses the measurements made of η from the NOE. It can be seen from these values that while the agreement between the calculated and the experimental results for acetonitrile is excellent, if we accept the value of Lyerla et al., the agreement for methyl iodide is only fair. It has been suggested that scalar coupling of the carbon-13 to the rapidly relaxing ^{127}I may also contribute to the relaxation rate of the carbon-13 in methyl iodide.[84] This could explain the difference between the calculated and experimental relaxation rates and NOE's. However, it is very difficult to measure the ^{13}C-I coupling constant because of the broad linewidth of the iodine line, so it cannot be definitely said that scalar coupling makes a significant contribution. It can be seen from Tables XII and XIII that the difference between the calculated relaxation rates for methyl iodide and acetonitrile lies almost entirely in difference between the spin-rotation contributions, which is due to differences in the spin-rotation coupling

constants for the two molecules. If the anisotropy of the chemical shift that we have assumed for $^{13}CH_3CN$ is incorrect, if $\Delta\sigma$ is smaller than - 20 ppm or has a positive value, then the values for the spin-rotation coupling constants would be closer, although the excellent agreement between theory and experiment for methyl iodide would be lost.

III. MOLECULAR MOTION AND CARBON-13 SPIN-LATTICE RELAXATION TIMES IN LIQUID n-ALKANES

1. Introduction

The impetus for the calculations described in this part is the need to understand the molecular motion in the interior of the lipid bilayers which are a major component of cell membranes. These lipids consist of two alkane chains, which may be partially unsaturated, of 16-20 carbons attached to a polar head group. When they are dispersed in aqueous solution, the lipids aggregate into bilayers, with the polar head groups on the outside facing the aqueous medium and the methylene chains on the inside. The motion of these chains is important not only in terms of how it affects the transport of substances across the membrane, but also because the motion must influence the biochemical reactions which are known to take place within the bilayer.

Attempts have been made to characterize the chain motion using proton magnetic resonance, and transverse (T_2) and spin-lattice (T_1) relaxation times for the protons. Studies of the pmr linewidths of the methylene protons have been used to formulate a motional model in which there are two distinct chain motions[85]. (1), a relatively rapid motion about the chain axis, and (2), a slower

motion of the chain from side to side, which can be shown to be restricted to angles less than 60-70°. It might be thought that the proton spin-lattice relaxation times could be used to give a more quantitative picture of the motion, since T_1's can be related in a more direct manner to the motion. However, the methylene protons have been shown to relax primarily by spin-diffusion of the excess spin temperature to the fast-relaxing methylene protons near the end of the chain[86, 87], so that only the motion of the methyl groups can be deduced from T_1 measurements. When the model described above is used to interpret the T_1 value (~ .2 sec for unsonicated lecithin), values for the correlation times about the methyl top axis and perpendicular to it of about 10^{-10} sec and 10^{-7} sec, respectively, are obtained.[85, 87] Since these methylene groups are moving faster than the other methylene groups, these values would seem to represent upper limits for the chain motion. However, the interpretation of the proton relaxation rate is complicated by the presence of intermolecular dipolar coupling. It has been estimated that, for the terminal methyl group protons of sonicated dipalmitoyllecithin vesicles in D_2O solution, the intermolecular dipolar contribution to the relaxation rate is comparable to the intramolecular contribution.[88]

It is obvious from the discussion of Part II that neither spin-diffusion nor intermolecular dipolar coupling will be important

for the carbon-13 nuclei of the methylene chain. Furthermore, since carbon-13 nuclei have a much wider range of chemical shifts (~ 200 ppm) than do protons, and since the linewidths of the carbon-13 resonances tend to be narrower than those of protons (carbon-13 T_2's are longer), the individual carbon-13 methylene resonances are much easier to resolve than those of the protons. These considerations make the measurement of carbon-13 relaxation rates a promising endeavor. The results for alkane chain molecules which have been obtained to date are given in Table XIV. It can be seen from these results that the carbons near the methyl end of the chains have similar T_1's. However, except for qualitative statements to the effect that the motion of the chain is fastest at the methyl end, little has been done to interpret these results. Nevertheless, useful information has been obtained from these and related measurements. For example: (1) Octanol T_1's, measured in a solution containing enough polyvinylpyrrolidone to increase the viscosity by a factor of $\sim 10^3$, were less than 10% different from those measured in neat solution,[90] indicating that the internal chain motion essentially determines the relaxation rate; (2) T_1's measured for fluorine labeled lecithins showed practically no change from those of unlabeled lecithin, and T_1's for lecithin containing a double bond (at C_9) showed small changes ($< 20\%$), but

Table XIV. Carbon-13 Spin-Lattice Relaxation Rates for Molecules Containing Methylene Chains.

Decanol		Octanol		DPL	
C#	T_1 (sec)	C#	T_1 (sec)	C#	T_1 (sec)
10	3.1	8	4.05	16	3.34
9	2.2	7	2.80	15	1.81
8	1.6	6	2.12	14	1.13
7	1.1	5	1.64	4-13	.53 (unresolved)
6	.84	4	1.35	3	.22
5	.84	3	1.35	2	.10
4	.84	2	1.15	1	
3	.77	1	.87		
2	.77				
1	.65				

Experimental Conditions

Decanol: Ref. (89), 42° C, neat solution, 15.08 MHz.

Octanol: Ref. (90), 38° C, neat solution, 25.2 MHz.

Dipalmitoyllecithin (DPL): Refs. (91), (92), 52° C, sonicated vesicles in D_2O solution, 25.2 MHz.

those for spin-labeled lecithin differed greatly from the unlabeled lecithin;[92] (3) T_1's measured for DPL in CD_3OD and $CDCl_3$ solution showed that while the changes in the degree of aggregation of the DPL molecules that are known to occur in these solvents produce T_1 increases of about a factor of two, the relaxation rates are still predominantly determined by the internal motion.[92]

Previous attempts to understand the internal motion of hydrocarbons have been made chiefly by chemists who want to understand the physical properties of high polymers, and their studies provide an obvious starting point for our analysis. However, since the properties of interest to polymer chemists are generally equilibrium thermodynamic quantities, the dynamics of the polymer motion, which we need to understand to calculate the nuclear magnetic relaxation rate, is generally not considered. In the treatment that follows, we will first deal with the purely alkane molecules that the statistical polymer models have been developed for, and then attempt to show how we would modify the treatment to correct for the restrictions on the motion which are present in the molecules (decanol, DPL) for which relaxation times have been measured. It might be thought that the motion of the end of the chain farthest away from the polar head group (in DPL) or the alcohol group (in decanol) will not be too different from that of a pure alkane chain.

2. Configuration Statistics of Alkane Chains

It is well known that the hindering potential for internal rotation in the ethane molecule has three minima 120° apart and is of the form[93]

$$U(\phi) = U_0/2\ (1 - \text{Cos}\ 3\phi) \qquad (1)$$

where ϕ is the angle of rotation measured from the staggered form of the molecule, and U_0 is the height of the potential barrier, and may be thought of as an activation energy for internal rotation. U_0 has been determined by several methods to be about 3.0 kcal/mole.[94] In propane, U_0 increases to 3.4 kcal/mole. When we look at the first alkane with a purely internal bond, n-butane, starting in the configuration in which all the carbons lie in a plane--the trans form--we see that a rotation about the C_2-C_3 internal bond brings the protons of the C_1 and C_4 carbons into closer proximity, so that the two other rotational states for which the C_2 and C_3 protons are staggered--the gauche forms--will have higher energies than the trans state. The energy difference between the trans and the gauche states has been determined using Raman Spectroscopy to be about 760 ± 100 cal/mole,[95] and U_0 is found to be about 3.6 kcal/mole. It will be noticed that the barriers to internal rotation for these molecules are large enough with respect to RT for normal temperatures so that a given bond can be

treated as being in one of three discrete rotational states, and a molecule can be described in terms of combinations of these states. Torsional oscillations of the bonds about the potential minima are assumed to be random, and thus have no effect on the average properties of the molecule. This model is what is usually referred to as the Rotational Isomeric State Approximation.[96] Raman studies for higher n-alkanes give smaller values for the trans-gauche energy difference: 450 ± 60 cal/mole for pentane, 520 ± 70 and 470 ± 60 cal/mole (two different experiments) for hexane.[97] The barrier to internal rotation for higher n-alkanes cannot be easily determined, but is usually assumed to be about 3.5 kcal/mole. Rotation between the two gauche states (which we designate as g and g′) without going through the trans state puts the adjoining carbons in a cis configuration. The barrier for this rotation has not been measured, but has been calculated to be between 10 and 11 kcal/mole.[98] The strong repulsions which occur as the cis configuration is approached indicate that the potential minima for the gauche states will probably occur at angles which are less than $\phi = \pm 120°$. When terms are added to Eqn. (1) to account for these repulsions, and the parameters involved are adjusted to fit the trans-gauche potential barriers for the shorter alkanes, the new potential function gives minima at 5-10° less than 120°.[98, 99] The trans-gauche energy difference is calculated to be

between 400 and 500 cal/mole for these potential functions. Furthermore, the physical properties of alkane polymers are best reproduced theoretically when values for the trans-gauche energy difference of about 400 cal/mole are used. We emphasize that for the specific situation we are interested in here--the rotational isomers of n-alkane--we can use the rotational state approximation to describe the conformations, but we must realize that the values for the energy difference and the activation energy between the states will be uncertain, particularly for the first few bonds.

If we apply the rotational isomeric state approximation to the internal bond in n-butane, the statistical weight u_g for each of the gauche states is

$$u_g = \sigma = e^{-E_\sigma/RT} \tag{2}$$

where E_σ is the energy of the gauche state with respect to the trans state. The internal rotation partition function will be

$$Z = 1 + \sigma + \sigma \tag{3}$$

For molecules which have more than one internal bond, the statistical weight for a given bond and a given state will depend on the states of the bonds before and after it. Longer range interactions (with bonds $i \pm 2$, etc.) are assumed not to be important. The statistical weight

for bond i in state α, given that bond i - 1 is in state β is written[94]

$$u_{\beta\alpha;\,i} = \exp\left(-E_{\beta\alpha;\,i}/RT\right) \tag{4}$$

These statistical weights form a β by α matrix for a given bond, designated $\underset{\sim}{U}_i = \left\{ u_{\beta\alpha} \right\}_i$. To find the partition function for the whole molecule, we must multiply these matrices together. The dependence of the state of bond i on the state of i + 1 will be taken into account when we write the matrix for bond i + 1. Further, for a homogeneous chain, all the matrices are taken to be identical. The partition function for a three state potential function for an n-alkane can be written[94]

$$Z = \vec{J}^{*} \left[\prod_{i=2}^{n-1} \underset{\sim}{U}_i \right] \vec{J} \tag{5}$$

where $\vec{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$ and $\vec{J}^{*} = [1\ 0\ 0]$. The zeroes in $\vec{J}^{*}$ allow for the fact that the states of bond i = 1 are indistinguishable from one another (we consider bond i = 1 when we write the matrix for bond i = 2). To consider the individual $\underset{\sim}{U}_i$, we write

$$\underset{\sim}{U}_i = \begin{bmatrix} u_{tt} & u_{tg} & u_{tg'} \\ u_{gt} & u_{gg} & u_{gg'} \\ u_{g't} & u_{g'g} & u_{gg'} \end{bmatrix} \tag{6}$$

where the first subscript (rows) gives the state of bond i - 1 and the second (columns) that of bond i. It is convenient to define a reference state for the energies $E_{\beta\alpha}$ which are associated with the $u_{\beta\alpha}$ in which all bonds are in their trans states. Using this convention means that $E_{\beta\alpha}$ is the energy of interaction produced when bond i is changed from the trans state to state α, i.e., when $\alpha = t$, then

$$E_{tt} = E_{gt} = E_{g't} = 0 \tag{7}$$

Furthermore,

$$\begin{aligned} E_{tg} &= E_{tg'} = E_{\sigma} \\ E_{gg} &= E_{g'g'} = E_{\sigma} + E_{\psi} \\ E_{gg'} &= E_{g'g} = E_{\sigma} + E_{\omega} \end{aligned} \tag{8}$$

where E_{ψ} and E_{ω} are the energies for a gg and a gg′ pair, respectively, in excess of that for a tg pair. We can therefore rewrite $\underset{\sim}{U}_i$

$$\underset{\sim}{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix} \tag{9}$$

If we now wish to calculate the probability that bond i is in state α, we can write[94]

$$p_{\alpha;i} = Z^{-1} \vec{J}^{*} \left[\prod_{h=2}^{i-1} \underset{\sim}{U}_h \right] \underset{\sim}{U}'_{\alpha,i} \left[\prod_{j=i+1}^{n-1} \underset{\sim}{U}_j \right] \vec{J} \tag{10}$$

where $\underset{\sim}{U}'_{\alpha;i}$ is the matrix obtained from $\underset{\sim}{U}_i$ by setting all elements equal to zero except those in column α. For a relatively short chain alkane, such as those we are interested in here, these probabilities can be easily calculated using a digital computer to multiply the matrices.

3. Dynamic Analysis of Internal Rotation[100,101]

In order to calculate the effect of the internal rotational motion about the individual bonds on the spin-lattice relaxation rate, we must calculate the probability per unit time that bond i undergoes a transition from state β to state α, $p_{\beta\alpha;i}$. We set up three differential equations for the time change of the concentration C_α of bonds in state α for an ensemble of bonds

$$\frac{dC_t}{dt} = -(p_{tg} + p_{tg'})\,C_t + p_{gt}C_g + p_{g't}C_{g'}$$

$$\frac{dC_g}{dt} = p_{tg}C_t - (p_{gg'} + p_{gt})\,C_g + p_{g'g}C_{g'} \qquad (11)$$

$$\frac{dC_{g'}}{dt} = p_{tg'}C_t + p_{gg'}C_g - (p_{g'g} + p_{g't})\,C_{g'}$$

We wish to solve for the conditional probability $P_{\beta\alpha}$, the probability that the bond is in state α at time t, given that it was in state β at t = 0. First, we notice that from the symmetry of the potential function $p_{gg'} = p_{g'g}$, $p_{gt} = p_{g't}$ and $p_{tg} = p_{tg'}$. Furthermore, at thermal equilibrium p_{gt} and p_{tg} must be related by the gauche to trans populations, i.e., $p_{tg} = (p_g/p_t)p_{tg} = Ap_{gt}$. Obviously the population ratio A can be calculated for each bond i using the method described in the previous section. If we define $x = p_{gt}$ and $y = p_{gg'}$, then we can rewrite Eqns. (11)

$$\frac{dC_t}{dt} = 2AxC_t + xC_g + xC_{g'}$$

$$\frac{dC_g}{dt} = AxC_t - (x+y)C_g + yC_{g'} \qquad (12)$$

$$\frac{dC_{g'}}{dt} = AxC_t + yC_g - (x+y)C_{g'}$$

To solve these equations we set up a determinant

$$D = \begin{vmatrix} -(2Ax + r) & x & x \\ Ax & -(x+y+r) & y \\ Ax & y & -(x+y+r) \end{vmatrix} = 0 \qquad (13)$$

and solve for the roots of the equation in r^2 that can be formed from D. These are $r = 0, -(x+2y), -x(2A+1)$, so that the general form of the solution is

$$C_\alpha = K_{\alpha 1} + K_{\alpha 2}e^{-(2A+1)xt} + K_{\alpha 3}e^{-(x+2y)t} \qquad (14)$$

Substituting the values for r back into the equations represented by the determinant D gives the relations among the K_α. We find

$$C_t(t) = K_1 - 2K_2 e^{-(2A+1)xt}$$

$$C_g(t) = AK_1 + K_2 e^{-(2A+1)xt} + K_3 e^{-(x+2y)t} \qquad (15)$$

$$C_{g'}(t) = AK_1 + K_2 e^{-(2A+1)xt} - K_3 e^{-(x+2y)t}$$

We can now put in the various initial conditions, and find the $P_{\beta\alpha}$. For $C_t(o) = 1$, $C_g(o) = C_{g'}(o) = 0$, we find

$$P_{tt} = \frac{1}{2A+1}\left(1 + 2A\, e^{-(2A+1)xt}\right)$$

$$P_{tg} = P_{tg'} = \frac{A}{2A+1}\left(1 - e^{-(2A+1)xt}\right) \qquad (16)$$

For $C_t(o) = 0$, $C_g(o) = 1$, $C_{g'}(o) = 0$, we find

$$P_{gg} = P_{g'g'} = 1/2\left[\frac{1}{2A+1}\left(2A + e^{-(2A+1)xt}\right) + e^{-(x+2y)t}\right]$$

$$P_{gg'} = P_{g'g} = 1/2\left[\frac{1}{2A+1}\left(2A + e^{-(2A+1)xt}\right) - e^{-(x+2y)t}\right]$$

$$P_{gt} = P_{g't} = \frac{1}{2A+1}\left(1 - e^{-(2A+1)xt}\right) \qquad (17)$$

If we now substitute $A = p_g/p_t$ into these expressions, noticing that $2p_g + p_t = 1$, and defining the characteristic times τ_1 and τ_2 by $1/\tau_1 = (2A + 1)p_{gt} = p_{tg}/p_g$ and $1/\tau_2 = p_{gt} + 2p_{gg'}$, we can rewrite Eqns. (16 and 17)

$$
\begin{aligned}
P_{tt} &= p_t + 2p_g e^{-t/\tau_1} \\
P_{tg} &= P_{tg'} = p_g (1 - e^{-t/\tau_1}) \\
P_{gg} &= P_{g'g'} = 1/2\,(2p_g + p_t\ e^{-t/\tau_1} + e^{-t/\tau_2}) \\
P_{gg'} &= P_{g'g} = 1/2\,(2p_g + p_t\ e^{-t/\tau_1} - e^{-t/\tau_2}) \\
P_{gt} &= P_{g't} = p_t (1 - e^{-t/\tau_1})
\end{aligned}
\tag{18}
$$

4. Carbon-13 Spin-Lattice Relaxation Rate

Since carbon-13 and the proton are unlike spins, we cannot use Eqn. (43) from Section 4 of Part I for the intramolecular dipolar relaxation rate, but instead we must use[21]

$$R_1^{da} = \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{r^6} \left[\frac{1}{16} J_0 (\omega_C - \omega_H) + 9/8\, J_1 (\omega_C) + \frac{9}{16} J_2 (\omega_C + \omega_H) \right] \tag{19}$$

where

$$J_1 (\omega) = \int_{-\infty}^{\infty} \overline{F_i (t + \tau)\, F_i (t)}\, e^{i\omega\tau}\, dt \tag{20}$$

In our treatment of the motion of a methylene chain, we will follow closely the treatment of Woessner.[45] We wish to describe the motion of a C-H vector as it undergoes both internal motion and motion due to the movement of the axis of internal rotation. We define four angles to specify these motions: the fixed angle Δ between the C-H vector and the internal rotation axis, the variable azimuth of the C-H vector about the rotation axis, ϕ', and the angles θ and ϕ which describe the orientation of the rotation axis with respect to the external magnetic field $\vec{H}_0$. If we write direction cosines for these angles we can find[45]

$$F_0(t) = 1/2(3\ \mathrm{Cos}^2\ \Delta - 1)\ (1 - 3\ \mathrm{Cos}^2\ \theta)$$

$$+3\ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ \mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta\ e^{i\phi'} + 3\ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ \mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta\ e^{-i\phi'}$$

$$-3/4\ \mathrm{Sin}^2\ \Delta\ \mathrm{Sin}^2\ \theta\ e^{2i\phi'} - 3/4\ \mathrm{Sin}^2\ \Delta\ \mathrm{Sin}^2\ \theta\ e^{-2i\phi'} \qquad (21)$$

$$\begin{aligned} F_1(t) = [&1/2\ (3\ \mathrm{Cos}^2\ \Delta - 1)\ \mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta \\ &+ 1/2\ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ (\mathrm{Cos}^2\ \theta - \mathrm{Sin}^2\ \theta + \mathrm{Cos}\ \theta)e^{i\phi'} \\ &+ 1/2\ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ (\mathrm{Cos}^2\ \theta - \mathrm{Sin}^2\ \theta - \mathrm{Cos}\ \theta)e^{-i\phi'} \\ &- 1/4\ \mathrm{Sin}^2\ \Delta\ (\mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta + \mathrm{Sin}\ \theta)e^{2i\phi'} \\ &- 1/4\ \mathrm{Sin}^2\ \Delta\ (\mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta - \mathrm{Sin}\ \theta)e^{-2i\phi'}\ ]\ e^{i\phi} \end{aligned}$$

$$\begin{aligned} F_2(t) = [&1/2\ (3\ \mathrm{Cos}^2\ \Delta - 1)\ \mathrm{Sin}^2\ \theta \\ &+ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ (\mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta + \mathrm{Sin}\ \theta)e^{i\phi'} \\ &+ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ (\mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta - \mathrm{Sin}\ \theta)e^{-i\phi'} \\ &+ 1/4\ \mathrm{Sin}^2\ \Delta\ (1 + \mathrm{Cos}^2\ \theta + 2\ \mathrm{Cos}\ \theta)e^{2i\phi'} \\ &+ 1/4\ \mathrm{Sin}^2\ \Delta\ (1 + \mathrm{Cos}^2\ \theta - 2\ \mathrm{Cos}\ \theta)e^{-2i\phi'}\ ]\ e^{2i\phi} \end{aligned}$$

We now assume that the motion about the internal rotation axis is independent of the motion of the axis about $\vec{H}_0$, so that we can factor the $F_i(t)$ terms into two parts. For example, $F_0(t)$ can be written

$$F_o(t) = f_a g_a + f_b g_b + f_c g_c + f_d g_d + f_e g_e \tag{22}$$

where

$$\begin{aligned} f_a &= 1/2\ (3\ \mathrm{Cos}^2\ \Delta - 1)\ (1 - 3\ \mathrm{Cos}^2\ \theta) \\ f_b &= 3\ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ \mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta \\ f_c &= 3\ \mathrm{Sin}\ \Delta\ \mathrm{Cos}\ \Delta\ \mathrm{Sin}\ \theta\ \mathrm{Cos}\ \theta \\ f_d &= -3/4\ \mathrm{Sin}^2\ \Delta\ \mathrm{Sin}^2\ \theta \\ f_e &= -3/4\ \mathrm{Sin}^2\ \Delta\ \mathrm{Sin}^2\ \theta \end{aligned} \tag{23}$$

and

$$\begin{aligned} g_a &= 1 \\ g_b &= e^{i\phi'} \\ g_c &= e^{-i\phi'} \\ g_d &= e^{2i\phi'} \\ g_e &= e^{-2i\phi'} \end{aligned} \tag{24}$$

so that we can write

$$\overline{F_i(t+\tau)\,F_i(t)} = \sum_{j,k=a}^{e} \overline{f_j^*(t+\tau)\,f_k(t)}\ \ \overline{g_j(t+\tau)\,g_k(t)} \tag{25}$$

We now assume that the three state rotational isomeric model described in Sections 2 and 3 can be used to describe the reorientation of ϕ'. By analogy to Eqn. (46) of Section 4 of Part I, we write

$$\overline{g_j^* (t+\tau) g_k(t)} = \sum_{\alpha,\beta} p_\beta P_{\beta,\alpha} g_j^* (\beta) g_k (\alpha) \tag{26}$$

where p_β and $P_{\beta,\alpha}$ are defined as in Section 2 and 3. For the trans state we have $\phi' = \phi'_0$, and for the gauche states $\phi' = \phi'_0 \pm 2\pi/3$. As an example, we will calculate the g average for j = k = b

$$\begin{aligned}\overline{g_b^* (t+\tau) g_b(t)} &= p_t P_{tt} e^{-i\phi'_0} e^{i\phi'_0} \\ &+ p_t P_{tg} e^{-i\phi'_0} e^{i(\phi'_0 + 2\pi/3)} + p_t P_{tg'} e^{-i\phi'_0} e^{i(\phi'_0 - 2\pi/3)} \\ &+ p_g P_{gg} e^{-i(\phi'_0 + 2\pi/3)} e^{i(\phi'_0 + 2\pi/3)} + p_g P_{gt} e^{-i(\phi'_0 + 2\pi/3)} e^{i\phi'_0} \\ &+ p_g P_{gg'} e^{-i(\phi'_0 + 2\pi/3)} e^{i(\phi'_0 - 2\pi/3)} + p_{g'} P_{g'g'} e^{-i(\phi'_0 - 2\pi/3)} e^{i(\phi'_0 - 2\pi/3)} \\ &+ p_{g'} P_{g't} e^{-i(\phi'_0 - 2\pi/3)} e^{i\phi'_0} + p_{g'} P_{g'g} e^{i(\phi'_0 - 2\pi/3)} e^{i(\phi'_0 + 2\pi/3)}\end{aligned} \tag{27}$$

By substituting Eqns. (18) into this expression, using the symmetry relations between the $P_{\beta,\alpha}$ and doing the necessary algebra, we can find

$$\overline{g_b^*(t+\tau)\, g_b(t)} = R = (p_t - p_g)^2 + \frac{9}{2}\, p_t p_g\, e^{-t/\tau_1} + \frac{3}{2}\, p_g e^{-t/\tau_2} \qquad (28)$$

Similarly, we can find

$$\begin{aligned} \overline{g_a^*(t+\tau)\, g_a(t)} &= 1 \\ \overline{g_j^*(t+\tau)\, g_j(t)} &= R \text{ for } j = c, d, \text{ or } e \\ \overline{g_j^*(t+\tau)\, g_k(t)} &= 0 \text{ for } j \neq k \end{aligned} \qquad (29)$$

The fact that the cross-terms for the g averages vanish means that we need not consider the f averages. We further assume, as we did in Part I, that the f averages have the form

$$\overline{f_j^*(t+\tau)\, f_j(t)} = f_j^*(t)\, f_j(t)\, e^{-|\tau|/\tau_c} \qquad (30)$$

In doing these averages, we find, as before, that the $e^{i\phi}$ terms cancel. The functions of the angle θ are usually averaged over all values of θ. However, as discussed in Section 1, the proton T_1 and T_2 data for lecithin bilayers are consistent with a model for which θ is restricted in the values it can assume. For decane, on the other hand, it seems reasonable that θ will take on all values with equal probability. A molecule like decanol may represent some kind of intermediate case. For generality we will retain the averages in θ at this point. Doing

suitable manipulations, we can find

$$\overline{F_0^*(t+\tau)\,F_0(t)} = A\,\overline{(1 - 3\,\mathrm{Cos}^2\theta)^2}\,e^{-|\tau|/\tau_c} + 3B\,\overline{\mathrm{Sin}^2\theta\,\mathrm{Cos}^2\theta}\,e^{-|\tau|/\tau_c}\,R + 3/4\,C\,\overline{\mathrm{Sin}^4\theta}\,e^{-|\tau|/\tau_c}\,R \tag{31}$$

$$\overline{F_1^*(t+\tau)\,F_1(t)} = A\,\overline{\mathrm{Sin}^2\theta\,\mathrm{Cos}^2\theta}\,e^{-|\tau|/\tau_c} + B/6\,\overline{(2 - 5\,\mathrm{Sin}^2\theta + 4\,\mathrm{Sin}^4\theta)}\,e^{-|\tau|/\tau_c}\,R + C/6\,\overline{\mathrm{Sin}^2\theta\,(1 + \mathrm{Cos}^2\theta)}\,e^{-|\tau|/\tau_c}\,R$$

$$\overline{F_2^*(t+\tau)\,F_2(t)} = A\,\overline{\mathrm{Sin}^4\theta}\,e^{-|\tau|/\tau_c} + 2B/3\,\overline{\mathrm{Sin}^2\theta\,(1 + \mathrm{Cos}^2\theta)}\,e^{-|\tau|/\tau_c}\,R + C/6\,\overline{(1 + 6\,\mathrm{Cos}^2\theta + \mathrm{Cos}^4\theta)}\,e^{-|\tau|/\tau_c}\,R$$

where we have defined

$$A = 1/4\,(3\,\mathrm{Cos}^2\Delta - 1)^2$$
$$B = 3\,\mathrm{Sin}^2\Delta\,\mathrm{Cos}^2\Delta \tag{32}$$
$$C = 3/4\,\mathrm{Sin}^4\Delta$$

We can find the spectral densities $J_i(\omega)$ using Eqn. (20)

$$
\begin{aligned}
J_0(\omega_c - \omega_H) &= A\,\overline{(1 - 3\,\mathrm{Cos}^2\theta)^2}\;\frac{2\tau_c}{1 + (\omega_c - \omega_H)^2\tau_c^2} \\
&\quad + 3B\,\overline{\mathrm{Sin}^2\theta\,\mathrm{Cos}^2\theta}\;S(\omega_c - \omega_H) \\
&\quad + 3/4\;C\,\mathrm{Sin}^4\theta\;S(\omega_c - \omega_H) \\
J_1(\omega_c) &= A\,\overline{\mathrm{Sin}^2\theta\,\mathrm{Cos}^2\theta}\;\frac{2\tau_c}{1 + \omega_c^2\tau_c^2} \\
&\quad + B/6\;\overline{(2 - 5\,\mathrm{Sin}^2\theta + 4\,\mathrm{Sin}^4\theta)}\;S(\omega_c) \\
&\quad + C/6\;\overline{\mathrm{Sin}^2\theta\,(1 + \mathrm{Cos}^2\theta)}\;S(\omega_c) \\
J_2(\omega_c + \omega_H) &= A\,\mathrm{Sin}^4\theta\;\frac{2\tau_c}{1 + (\omega_c + \omega_H)^2\tau_c^2} \\
&\quad + 2B/3\;\overline{\mathrm{Sin}^2\theta\,(1 + \mathrm{Cos}^2\theta)}\;S(\omega_c + \omega_H) \\
&\quad + C/6\;\overline{(1 + 6\,\mathrm{Cos}^2\theta + \mathrm{Cos}^4\theta)}\;S(\omega_c + \omega_H)
\end{aligned}
\tag{33}
$$

where

$$S(\omega) = (p_t - p_g)^2 \frac{2\tau_c}{1+\omega^2\tau_c^2} + \frac{9}{2} p_t p_g \frac{2\tau_c}{1+\omega^2\tau_c^2} + \frac{3}{2} p_g \frac{2\tau_c}{1+\omega^2\tau_{c2}^2} \tag{34}$$

and $1/\tau_{c1} = 1/\tau_c + 1/\tau_1$, $1/\tau_{c2} = 1/\tau_c + 1/\tau_2$.

If the motion is not restricted, then we can find the angle averages

$$\overline{(1 - 3\,\mathrm{Cos}^2\theta)^2} = \frac{\int_0^\pi (1 - 3\,\mathrm{Cos}^2\theta)^2\, 2\pi\,\mathrm{Sin}\,\theta\,d\theta}{\int_0^\pi 2\pi\,\mathrm{Sin}\,\theta\,d\theta} = 4/5 \tag{35}$$

$$\overline{\mathrm{Sin}^2\theta\,\mathrm{Cos}^2\theta} = 2/15$$

$$\overline{\mathrm{Sin}^4\theta} = 8/15$$

$$\overline{(2 - 5\,\mathrm{Sin}^2\theta + 4\,\mathrm{Sin}^4\theta)} = 4/5$$

$$\overline{\mathrm{Sin}^2\theta\,(1 + \mathrm{Cos}^2\theta)} = 4/5$$

$$\overline{(1 + 6\,\mathrm{Cos}^2\theta + \mathrm{Cos}^4\theta)} = 16/5$$

If we further assume extreme narrowing, then

$$S(\tau) = 2(p_t - p_g)^2 \tau_c + 9\, p_t p_g \tau_{c_1} + 3\, p_g \tau_{c_2} \tag{36}$$

and

$$R_1^{da} = \frac{n_H \gamma_H^2 \gamma_c^2 \hbar^2}{r^6} \left[A\tau_c + \frac{19}{40} BS(\tau) + \frac{19}{40} CS(\tau) \right] \tag{37}$$

5. Calculations and Discussion

In this section we will attempt to show that the theory described above can predict the differences in the carbon-13 relaxation times along an alkane chain. However, the relaxation times for the molecule for which the theory was developed, n-decane, have not been measured, nor have they for any other n-alkane, to our knowledge. So we will compare our calculated results with the experimental relaxation times for the first few carbons of n-decanol, with the assumption that they will be close to those of decane, or at least that they will vary in the same direction and by comparable amounts. It should be stressed that these calculations are preliminary and inexact in the sense that several of the quantities needed for the calculations are not known exactly and must be guessed at, particularly the correlation time τ_c, which we have not attempted to characterize. It seems reasonable that an important factor in determining τ_c will be the effect of the internal rotation about a given bond on the motion of the carbons beyond the neighboring bonds, which we did not take into account

when we characterized the internal motion. Also, a good deal of the reasoning in this discussion is speculative in nature, and may obviously need to be modified or discarded at a later time. However, we believe that the model gives a reasonable physical picture of the internal motion of an alkane chain.

We have written a computer program using Eqn. (10) to calculate the probability $p_{g;i}$ that each bond i of decane is in a gauche state. As a first approximation, it was assumed that E_σ has a constant value of 500 cal/mole for all of the internal bonds, and that $E_\omega = 2.0$ kcal/mole and $E_\psi = 0$. These numbers have been used by other workers to do similar calculations on long chain alkanes.[94, 99] It is found that the probability for a gauche state decreases as one goes away from the end of the chain, and that the probability does not change perceptibly after the i = 5 bond is reached (for chains longer than decane). This behavior seems physically reasonable if one thinks in terms of increased interaction among the adjacent methylene groups as one moves away from the end of the chain. However, when a constant value for E_σ along the chain is assumed, the value for p_g for i = 3 is anomalous, i.e., it is lower than the values for i = 4 or 5. This situation will cause a similar anomaly in T_1 for the carbon-13's, if Eqns. (36) and (37) are used to calculate the relaxation time. The measured values for E_σ cited in Section 1 indicate that there may be

an anomaly in E_σ as one goes along the chain, which may be the result of two opposing trends: one which lowers E_σ because of the shift in the angle at which the gauche states occur, and one that increases E_σ because of increased steric hindrance from neighboring methylenes. At any rate, if we assume that there is a small anomaly in E_σ, then the anomaly in p_g disappears, as shown by the following data for decane:

Bond #	2	3	4	5	6	7	8
E_σ(cal/mole)	500	450	475	500	475	450	500
p_g	.208	.187	.186	.181	.186	.187	.208

Without making any claims as to the reliability of these probabilities, we will use them to calculate the carbon-13 relaxation times.

We estimate the probability for a trans to gauche transition using the expression[101]

$$p_{tg} \cong \nu = \nu_0 e^{-E_a/RT} \tag{38}$$

where ν is the number of trans-gauche jumps per second, ν_0 is the torsional frequency about a C-C bond, and E_a is the barrier to rotation. For ethane $\nu_0 = 275\ cm^{-1} = 8.25 \times 10^{12}$ Hz. Since this value depends mostly on the shape of the potential function near its minimum,

it is usually assumed that it remains constant as one goes away from the end of the chain, and that it is the same for the trans and gauche states. If we assume a value for E_a of 3.4 kcal/mole, then we find at 42° C,

$$p_{tg} = 8.23 \times 10^{12}\, e^{-3400/RT} = 3.61 \times 10^{10}\ \text{sec}^{-1}.$$

As mentioned in Section 1, the $g \rightarrow g'$ barrier has been estimated to be about 10 kcal/mole. This value gives $p_{gg'} = 9.50 \times 10^{5}\ \text{sec}^{-1}$. This motion will be too slow to affect the spin-lattice relaxation time, so we will ignore its effect. Therefore for the second carbon of decane ($p_g = .208$),

$$\tau_1 = p_g/p_{tg} = .576 \times 10^{-11}\ \text{sec}$$

$$\tau_2 = \frac{1}{p_{gt} + p_{gg'}} \cong \frac{1}{p_{gt}} = \frac{p_g}{p_t p_{tg}} = .987 \times 10^{-11}\ \text{sec}\ .$$

We use a value for the C-H bond distance of 1.12 A[102] to calculate

$$\frac{n_H \gamma_c^2 \gamma_H^2 \hbar^2}{r^6} = 3.65 \times 10^{10}\ \text{sec}^2$$

and a value for Δ of 109.5°[102] to find,

$$A = 1/4\ (3\ \mathrm{Cos}^2\ \Delta - 1)^2 = .111$$

$$B = 3\ \mathrm{Sin}\ \Delta\ \mathrm{Cos}^2\ \Delta = .297$$

$$C = 3/4\ \mathrm{Sin}^4\ \Delta = .592\ .$$

Using Eqn. (37) for R_1 gives

$$R_1 = 3.65 \times 10^{10}\ [\,.111\ \tau_c + .422\ S(\tau)].$$

From Eqn. (36) for $S(\tau)$ we have,

$$S(\tau) = \left[\,.282 + \frac{1.089\tau_1}{\tau_c + \tau_1} + \frac{.624\tau_2}{\tau_c + \tau_2}\right]\ \tau_c\ .$$

Using the measured value for T_1 for the second carbon of decanol ($T_1 = 2.2$ sec) and the values for τ_1 and τ_2 from Eqn. (39), we can calculate a value for τ_c of 3.54×10^{-11} sec. To check our theory we use this value of τ_c and a probability $p_g = .187$ to calculate a value for T_1 for the third carbon of decanol. We find $S(\tau) = 2.28 \times 10^{-11}$ sec and $R_1 = .495\ \mathrm{sec}^{-1}$ ($T_1 = 2.02$ sec). This has changed in the right direction, but it is in only fair agreement with the measured value of 1.6 sec. However, we have assumed that the activation energy for internal rotation remains constant along the chain. It seems physically reasonable that the activation energy will increase as one

goes away from the end of the chain. For example, if we increase E_a to 3.6 kcal/mole for the third carbon, then we calculate $T_1 = 1.87$ sec, which is in somewhat better agreement with experiment. We maintain that, despite the discrepancies which still exist between experiment and theory, our theory gives an accurate picture of the internal motion of an alkane chain, particularly in view of the uncertainties involved in estimating the E_σ's and E_a's along the chain, and assuming τ_c is constant without attempting to characterize it.

As an exercise, we attempt to calculate τ_c for the overall motion of decanol using the Debye theory given in Part II. If we assume decanol is a cylinder, and measure its dimensions in the all trans form, we find h = 15.5 A, r = 2.3 A and $V_m = \pi r^2 h = 256.7\ A^3$. We calculate the microviscosity factor $f_\perp$ for motion about the chain axis using

$$f_\perp = [\, 6a/a_\perp + (1 + a/a_\perp)^{-3}]^{-1}$$

where $a_\perp = r = 2.3$ A and a = 3.95 (calculated from $a = (3\ V_m/4\pi^2)^{1/3}$). We find τ_c using

$$\tau_c = \frac{V_m \eta f_\perp}{kT} = 3.60 \times 10^{-11} \text{ sec.}$$

This is in very good agreement with the value of 3.54×10^{-11} sec found

from the T_1 value. But the agreement may be merely fortuitous, particularly in the light of the results obtained for octanol when the macroscopic viscosity is increased, as discussed in Section 1, and because of our supposition that τ_c will be mostly determined by the effects of the internal rotations on carbons farther along the chain. Obviously, a great deal of work remains to be done on the characterization of the motion responsible for τ_c.

REFERENCES

1. A. Carrington and A. D. McLachlan, Introduction to Magnetic Resonance, Harper and Row, New York, 1967.
2. C. P. Slichter, Principles of Magnetic Resonance, Harper and Row, New York, 1963.
3. F. Bloch, Phys. Rev., 70, 460 (1946).
4. N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev., 73, 679 (1948).
5. M. D. Zeidler, Ber. Bunsenges. Physik. Chem., 69, 659 (1965).
6. H. G. Hertz, Progr. NMR Spectry., 3 (1967) Chap. 5.
7. (a) H. S. Gutowsky, I, J. Lawrenson and K. Shimomura, Phys. Rev. Letters, 6, 349 (1961); (b) R. J. C. Brown, H. S. Gutowsky and K. Shimomura, J. Chem. Phys., 38, 76 (1963).
8. D. W. Aksnes, M. Rhodes and J. G. Powles, Mol. Phys., 14, 333 (1968).
9. W. T. Huntress, J. Chem. Phys., 48, 3524 (1968).
10. W. T. Huntress, Adv. Magn. Resonance, 4, 1 (1970).
11. T. T. Bopp, J. Chem. Phys., 47, 3621 (1967).
12. D. Wallach and W. T. Huntress, J. Chem. Phys., 50, 1219 (1969).
13. W. T. Huntress, J. Phys. Chem., 73, 103 (1970).
14. K. T. Gillen, M. Schwartz and J. H. Noggle, Mol. Phys., 20, 899 (1971).
15. A. A. Maryott, T. C. Farrar and M. S. Malmberg, J. Chem. Phys., 54, 64 (1971).
16. K. T. Gillen, D. C. Douglass, M. S. Malmberg and A. A.

Maryott, J. Chem. Phys., 57, 5170 (1972).

17. N. F. Ramsey, Phys. Rev., 78, 699 (1950); 86, 243 (1952); Am. Scient., 49, 509 (1951).
18. R. Schwartz, Ph. D. Thesis, Harvard University, 1953, unpublished.
19. R. Freeman and H. D. W. Hill, J. Chem. Phys., 54, 3367 (1971).
20. W. M. Litchman and M. Alei, J. Chem. Phys., 56, 5818 (1972).
21. A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, London, 1961, Chap. VIII.
22. P. Debye, Polar Molecules, Chemical Catalog Co., New York, 1929.
23. E. Wigner, Group Theory and Its Applications to the Quantum Mechanics of Atomic Spectra, Academic Press, New York, 1959.
24. E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, New York, 1969.
25. H. M. McConnell and C. H. Holm, J. Chem. Phys., 25, 1289 (1956).
26. P. S. Hubbard, Phys. Rev., 131, 1155 (1963).
27. P. W. Atkins, Mol. Phys., 12, 133 (1967); R. E. D. McClung and D. Kivelson, J. Chem. Phys., 49, 3380 (1968).
28. A. S. Dubin and S. I. Chan, J. Chem. Phys., 46, 4533 (1967).
29. T. E. Burke, Ph. D. Thesis, California Institute of Technology, 1968, unpublished; T. E. Burke and S. I. Chan, J. Mag. Resonance, 2, 120 (1970).
30. R. H. Cole, J. Chem. Phys., 42, 637 (1965).

31. W. A. Steele, J. Chem. Phys., 38, 2404 (1963); 38, 2411 (1963); W. B. Moniz, W. A. Steele and J. A. Dixon, J. Chem. Phys., 38, 2418 (1963).

32. E. N. I vanov, Soviet Phys. --- JETP, 18, 1041 (1964).

33. See, for example, Ref. (6) and R. J. Meakins, Trans. Faraday Soc., 54, 1160 (1958).

34. A. Gierer and K. Wirtz, Z. Naturforsch., 8a, 532 (1953).

35. N. E. Hill, Proc. Phys. Soc. (London), B67, 149 (1954).

36. E. M. Andrade, Phil. Mag., 17, 497, 698 (1934).

37. R. J. Meakins, Proc. Phys. Soc. (London), 72, 283 (1958).

38. T. E. Burke and S. I. Chan, J. Mag. Resonance, 3, 55 (1970).

39. K. T. Gillen and J. H. Noggle, J. Chem. Phys., 53, 801 (1970).

40. J. G. Powles, Ber. Bunsenges. Physik. Chem., 67, 328 (1963).

41. P. S. Hubbard, Phys. Rev., 131, 275 (1963).

42. A. S. Dubin, Ph. D. Thesis, California Institute of Technology, 1967, unpublished.

43. J. Karle and L. Brockway, J. Amer. Chem. Soc., 66, 574 (1944).

44. P. S. Hubbard, Phys. Rev., 109, 1153 (1958); 128, 650 (1962).

45. D. E. Woessner, J. Chem. Phys., 36, 1 (1962).

46. S. I. Chan and A. S. Dubin, J. Chem. Phys., 46, 1745 (1967).

47. A. B. Harris, E. Hunt and H. Meyer, J. Chem. Phys., 42, 2851 (1965).

48. See M. M. Kreevoy and P. H. Mead, Disc. Faraday Soc., 39, 166 (1965), and the General Discussion following this paper on p. 176, for a summary of the work done on the dissociation of

CF_3COOH. See also G. C. Hood, O, Redlich and C. A. Reilly, J. Chem. Phys., 23, 2229 (1955), for details of the nmr measurements.

49. C. C. Costain and G. P. Spivastava, J. Chem. Phys., 41, 1620 (1964).

50. A. Olivson, E. Lippmaa and J. Past, Eisti NSF Tead. Akad. Toim., Fuss.-Matem., 16, 390 (1967).

51. D. E. Jones, Ph. D. Thesis, University of California, Berkeley, 1970, unpublished; H. Sternlicht, private communication.

52. R. G. Parker and J. Jonas, J. Mag. Resonance, 6, 106 (1972).

53. I. Ozier, L. M. Crapo and N. F. Ramsey, J. Chem. Phys., 49, 2314 (1968).

54. W. N. Huo, J. Chem. Phys., 43, 624 (1965).

55. R. Ettinger, P. Blume, A. Patterson and R. C. Lauterbur, J. Chem. Phys., 33, 1957 (1960).

56. H. Spiesecke and W. G. Schneider, J. Chem. Phys., 35, 722, 731 (1961).

57. P. C. Lauterbur, J. Amer. Chem. Soc., 83, 1838 (1961).

58. H. Jaeckle, U. Haberlen and D. Schweitzer, J. Mag. Resonance, 4, 198 (1971).

59. H. D. W. Hill and R. Freeman, private communication.

60. W. H. Flygare and V. W. Weiss, J. Chem. Phys., 45, 2785 (1966).

61. P. C. Lauterbur, J. Chem. Phys., 27, 217 (1957).

62. H. S. Gutowsky and D. E. Woessner, Phys. Rev., 104, 843 (1956).

63. Ref. 7b, footnote 19.

64. P. Rigny and J. Virlet, J. Chem. Phys., 47, 4645 (1967).

65. S. I. Chan, J. Chem. Phys., 47, 1191 (1967).

66. A. Pines, W. K. Rhim and J. S. Waugh, J. Chem. Phys., 54, 5438 (1971).

67. R. A. Assink and J. Jonas, J. Phys. Chem., 73, 2445 (1969).

68. H. W. Spiess, D. Schweitzer, U. Haberlen and K. H. Hausser, J. Mag. Resonance, 5, 101 (1971).

69. R. R. Shoup and D. L. Van der Hart, J. Amer. Chem. Soc., 93, 2053 (1971).

70. T. E. Bull, J. S. Barthel and J. Jonas, J. Chem. Phys., 54, 3663 (1971).

71. C. S. Yannoni and H. Bleich, J. Chem. Phys., 55, 5406 (1971).

72. T. D. Alger and D. M. Grant, J. Phys. Chem., 57, 2538 (1971).

73. M. Eisner and R. W. Mitchell, Bull. Am. Phys. Soc., 6, 363 (1961).

74. E. Bonera and A. Rigamonti, J. Chem. Phys., 42, 171 (1965).

75. J. G. Powles and R. Figgins, Mol. Phys., 10, 155 (1966).

76. T. E. Bull and J. Jonas, J. Chem. Phys., 52, 4553 (1970).

77. D. E. Woessner, J. Chem. Phys., 40, 2341 (1964); D. E. O'Reilly, J. Chem. Phys., 53, 850 (1970).

78. K. F. Kuhlmann, D. M. Grant and R. K. Harris, J. Chem. Phys., 52, 3439 (1970).

79. E. R. Andrew and R. G. Eades, Proc. Roy. Soc. (London), A218, 537 (1953).

80. D. E. Woessner, B. S. Snowden and E. T. Strom, Mol. Phys., 14, 265 (1968); K. T. Gillen and J. H. Noggle, J. Chem. Phys., 53, 801 (1970).

81. C. S. Yannoni and E. B. Whipple, J. Chem. Phys., 47, 2508 (1967).

82. J. R. Lyerla, D. M. Grant and R. K. Harris, J. Phys. Chem., 75, 585 (1971).

83. T. C. Farrar, S. J. Druck, R. R. Shoup and E. D. Becker, J. Amer. Chem. Soc., 94, 699 (1972).

84. K. T. Gillen, M. Schwartz and J. H. Noggle, Mol. Phys., 20, 899 (1971).

85. C.H.A. Seiter and S.I. Chan, J. Amer. Chem. Soc., accepted for publication.

86. K. van Putte, J. Mag. Resonance, 2, 216 (1970).

87. G. Feigenson and S.I. Chan, J. Amer. Chem. Soc., manuscript in preparation.

88. A.G. Lee, N.J.M. Birdsall and J.C. Metcalfe, Biochemistry, 12 1650 (1973).

89. D. Doddrell and A. Allerhand, J. Amer. Chem. Soc., 95, 1558 (1971).

90. G.C. Levy, Proceedings of the 9th Colloquium on NMR Spectroscopy, Aachen, Germany, March, 1973.

91. J.C. Metcalfe, N.J.M. Birdsall, J. Feeney, A.G. Lee, Y.K. Levine, and P. Partington, Nature, 233, 199 (1971).

92. Y.K. Levine, N.J.M. Birdsall, A.G. Lee and J.C. Metcalfe, Biochemistry, 11, 1416 (1972).

93. J.D. Kemp and K.S. Pitzer, J. Chem. Phys., 4, 749 (1936); J. Amer. Chem. Soc., 59, 276 (1937).

94. P.J. Flory, Statistical Mechanics of Chain Molecules, Interscience, New York, 1969.

95. G.J. Szaz, N.B. Sheppard and D.H. Rank, J. Chem. Phys., 16, 704 (1948).

96. M.V. Volkenstein, Configurational Statistics of Polymeric Chains, Interscience, New York, 1963.

97. N. Sheppard and G.J. Szaz, J. Chem. Phys., 17, 86 (1949).

98. R.A. Scott and H.A. Scheraga, J. Chem. Phys., 44, 3054 (1966).

99. A. Abe, R.L. Jernigan, and P.J. Flory, J. Amer. Chem. Soc., 88, 631 (1966).

100. J.D. Hoffman and H.G. Pfeiffer, J. Chem. Phys., 22, 132 (1954); J.D. Hoffman, J. Chem. Phys., 23, 1331 (1955).

101. K.-J. Liu and R. Ullman, J. Chem. Phys., 48, 1158 (1968).

102. L.S. Bartell and D.A. Kohl, J. Chem. Phys., 39, 3097 (1963).